REPORT

Sediment studies in the Stockholm archipelago 2008

For Swedish Environmental Protection Agency

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3 March 2009

Archive number: U2519

The report approved:
3 March 2009

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Förord (Preface in Swedish)

IVL Svenska Miljöinstitutet AB erhöll under 2008 två uppdrag från Naturvårdsverket att undersöka bottnarna i Stockholms skärgård för att tillföra kunskap till två nationellt prioriterade forskningsområden:

- fördjupad analys av orsakerna till laminerade sediment och syrefria bottnar och deras återhämtning
- den interna omsättningen av fosfor – kvantitativa och kvalitativa studier av fosfors fastläggning respektive frisättning i sedimenten under olika syreförhållanden.

Denna rapport är en sammanställning och försök till tolkning av de sedimentundersökningar som utförts i sammanlagt 21 fjärdar i Stockholms inner, mellan och ytterskärgård.

Syftet med undersökningarna har varit att:

- undersöka utbredningen av laminerade sediment, syrgasfria bottnar och förekomsten av bottendjur i ett antal tidigare välundersökta fjärdar
- bedöma hur stora arealer som vid tiden för undersökningarna hade ansträngda syrgasförhållanden och jämföra detta med historiska data
- belysa om det föreligger någon skillnad i hur resultat från bottenfauna- respektive sedimentundersökningar från samma områden tolkas
- kartlägga förråd och flöden av rörlig fosfor i olika sediment
- undersöka mekanismer som styr fastläggning och läckage av fosfor i sediment

Rapporten har sammanställts vid IVL Svenska Miljöinstitutet AB, av tekn. lic. Magnus Karlson, IVL, tekn. Dr Mikael Malmaeus, IVL, professor Per Jonsson Stockholms universitet och fil. Dr Emil Rydin, Uppsala universitet.
Vi vill tacka Christer Lännergren, Stockholm Vatten och Anders Stehn, Eurofins Environment Sweden AB för tillhandahållande av data från Stockholm stads recipientkontrollprogram, Helena Enderskog, Mia Arvidsson och Kurt Pettersson, Erkenlaboratoriet för utförandet av sedimentkemiska analyser, Dan Lindgren, Uppsala universitet, för kartframställning. Gunnar Andersson, Statens veterinärmedicinska anstalt, Lennart Norell Sveriges lantbruksuniversitet och Magnus Rahmberg, IVL tackas för statistisk vägledning. Rahmberg tackas också tillsammans med CG Velin, Exeter KB för assistans under fältarbetet. Vi tackar också Emma Henningsson, Excellent English och Anders Jönsson, IVL för granskning samt Anna-Lisa Broström, IVL för redigering av manuskriptet. Slutligen vill vi tacka Lars Håkanson, Uppsala universitet för värdefulla diskussioner under arbetets gång.

Fotografiet på framsidan, Per Jonsson ©, togs dagarna innan den sista provtagningen utfördes i december 2008 och visar undersökningsbåten Perca till kaj vid Vindö. Båten har tjänstgjort som huvudsaklig provtagningsplattform i föreliggande studie.

Stockholm i februari 2009

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Summary

Background

Alarm reports related to eutrophication of the Baltic Sea, such as increased frequency of algae blooms, increasing areas with hypoxia and decreasing populations of predatory fish, have led to a public awareness of the fragility of the ecosystem and to a demand for remedial actions.

One of the more marked phenomenon associated with eutrophication is oxygen depletion, which sometimes occurs along seabeds where organic matter settles and mineralizes. In many marine and freshwater ecosystems there is a diversified and dense macrozoobenthos community within the top layer of the sediments. If the oxygen level decreases below a critical value there is a succession from animals towards bacteria capable of living under anaerobic conditions.

Oxygen depletion along seabeds has also for many years been recognized as an important factor behind an inefficient burial of phosphorus. Phosphorus is a necessary nutrient for algae production. However, for many years nitrogen was considered to be the nutrient that limits the primary production in the Baltic Sea, while phosphorus was considered to be of secondary importance. Findings in recent years indicate, however, that the opposite is the case. Therefore the present remediation strategy for the Baltic Sea focuses on phosphorus input reductions. Some scientists have also proposed that the deep sea sediments in the Baltic Sea should be aerated artificially in order to enhance phosphorus precipitation.

Several sedimentological surveys in the Stockholm archipelago during the 1990s showed surprisingly that despite marked improvements in the water quality after the installation of tertiary waste water treatment at sewage treatment plants (STPs) in the Lake Mälaren catchment area during the 1970s, large areas of the archipelago seabed were hypoxic. However, a contradicting picture of the situation on the seabeds of the inner archipelago could be seen in the results of the environmental monitoring programme of the City of Stockholm. From the middle of the 1990s onwards, these investigations have shown a gradually improving status of the macrozoobenthos community.

Methods

In the presented study we have repeated the sedimentological sampling excursions from the Stockholm archipelago in the 1990s. We have compared the results from our investigation with the old results. In the inner archipelago we have also compared the sedimentological results with equivalent measurements of macrozoobenthos. Moreover, in four selected areas from the inner, middle and outer archipelagos we have studied the phosphorus dynamics and forms within the sediments. The store of inert and mobile phosphorus has been estimated and the magnitude of sedimentation, turnover, leakage and burial has been calculated.

Results

It is with pleasure that we can state that the results indicate a marked improvement of the oxygen conditions along the seabeds of the inner and middle Stockholm archipelagos. In a majority of the investigated areas the surface sediments were oxidized and signs of bioturbation were noticeable. In the 1990s these areas were predominated by black and laminated surface sediments. Where it was possible to compare the interpretation of sediment status versus macrozoobenthos data an overwhelming congruence was found. The areas with black and laminated surface sediments also had an impoverished benthic animal community.

We hypothesised that the observed improvement of the benthic status in the inner archipelago was due to one or a combination of the following factors: 1) Reduced input of nutrients from land based sources; 2) reduced input of nutrients through water exchange from the outer archipelago; 3) Successive decay and removal of historical discharges that have been stored within the sediments and/or 4) a change in wind climate during the last decade resulting in increased turbulence and hence more efficient oxygenation of bottom waters.

Amongst other tools for evaluation, we used dynamic mass balance modelling to simulate and quantify the fluxes of water and matter through the inner archipelago. Our results indicate that the most important factor behind the observed improvement is the breakdown and/or removal of historical deposits within the sediments resulting in a reduced leakage of nutrients from the sediments to the water column. However, there is still a considerable leakage of nutrients from the sediments although this has decreased during the last decade. The nutrient transports from Lake Mälaren, the City of Stockholm STPs and the input from the outer archipelago have also decreased during the last decade.

In the middle archipelago we also found marked improvements of the benthic conditions in a number of sites compared to the situation a decade ago. These areas have been less affected by the input from the Lake Mälaren valley. The observed improvement in this case could instead be a result of an overall improvement of the Baltic Sea environmental conditions. However, to be able to test this hypothesis it would be necessary to expand the investigations to other areas along the coast of Sweden proper.

The magnitude of sediment phosphorus (P) turnover in the Stockholm archipelago is closely linked to the sediment accumulation rate. Improvement of the oxygen status in the surface sediment layer results in a temporary accumulation of iron (Fe) bound P. This P might reach high concentrations, and represents a withdrawal of P that otherwise would support primary production. Whether this Fe-P mainly precipitated in the water column and settled to the sediment, or whether it formed in the oxygenated surface sediment layer due to diffusion of dissolved P and Fe from deeper sediment layers remains uncertain.

In cores from Gälnan, Bullerö-, Torsby-, and Pilkobbsfjärden, gross deposition of P varied between less than 3 to near 5 $g \cdot m^{-2} \cdot yr^{-1}$, after correction for Fe-P accumulation. Burial concentrations of P occurred after between 2 and 10 years, and burial fluxes were measured to between 1.5 and 3 $g\ P \cdot m^{-2} \cdot yr^{-1}$. Sediment mobile P, mainly organic P and Fe-P, varied between less than 2 and up to 19 $g \cdot m^{-2}$. P to be released was calculated using two different approaches and yearly release rates between 0.2 and 2 $g\ P \cdot m^{-2}$ were obtained. These rates should be considered as minimum rates. The concentration and composition of P settling out from the water column during different seasons and at different sites needs to be determined to improve our estimates of P turnover in the archipelago. The redox sensitive P pools varied between around 0.2 and 14 $g \cdot m^{-2}$ (a factor of 60) reflecting alternative distributions of phosphorus between water and sediment. Extrapolated to the entire archipelago, it is likely that the accumulation sediments contain several thousand tonnes of mobile phosphorus.

All examined sediments appear to be net sinks of phosphorus. This does not exclude however, the possibility that sediments locally may act as temporary net sources of phosphorus, as indicated by mass-balances. To support such a suggestion, however, requires further studies in a larger sampling area, including sediments from a range of water depths and bottom dynamics. This study has not been complete enough to confidently establish the present quantitative influence of the archipelago sediments on the phosphorus dynamics of the water column. However, there are clear indications of a positive development.

Sammanfattning (Swedish Summary)

Bakgrund

I takt med att larmrapporter om frekventa algblomningar, ökad utbredning av döda bottnar, minskande bestånd av rovfisk, förändringar i makrovegetationens sammansättning mm. under senare år duggat tätt har samhället börjat ställa krav på att åtgärder genomförs som väsentligt förbättrar miljöförhållandena i Östersjön.

Ett av de mer påtagliga fenomen som kan kopplas till övergödning är den syrgasbrist som ibland uppstår längs bottnar där sedimenterande organiskt material ackumuleras och bryts ned. I många marina och limniska miljöer finns i de översta sedimentlagren längs mjukbottnar ett diversifierat och individrikt organismsamhälle. Om syrgasnivån varaktigt underskrider en kritisk nivå elimineras emellertid förutsättningarna för djurliv och det sker en succession mot bakterier som förmår leva under anaeroba förhållanden. Detta innebär att fisk och mobila bottenlevande djur lämnar området medan djur som saknar förmåga till längre förflyttningar slås ut.

Ansträngda syrgasförhållanden längs bottnar har sedan lång tid tillbaka också ansetts kunna leda till en försämrad fastläggning av näringsämnet fosfor. Fosfor är ett av de näringsämnen som algerna behöver för sin tillväxt. Under ganska lång tid ansågs emellertid fosfors betydelse i Östersjön vara underordnad förekomsten av kväve, som också är ett essentiellt näringsämne för alla organismer. Senare års forskning har dock snarare pekat på motsatsen och den tidigare strategin att i första hand minska tillförseln av kväve är numer ersatt av en rekommendation att fokusera reningsåtgärderna mot fosfor. Vissa forskare anser också att det skulle vara önskvärt att på artificiell väg försöka syresätta Östersjöns bottenvatten och på så sätt öka fastläggningen av fosfor i sedimenten.

Vid flera sedimentologiska undersökningar i Stockholms skärgård som genomfördes under 1990-talet förvånades man över att de påtagliga förbättringar av vattenkvaliteten som noterades i vattenmassan efter att förbättrad reningsteknik infördes under 1970-talet, resulterande i kraftigt minskad tillförsel av näringsämnen från Stockholm och Mälardalen, inte återspeglades i successivt förbättrade miljöförhållanden längs bottnarna. Tvärtom fann man att omfattande försämringar av bottenförhållandena skett under samma tidsepok som reningsverksutbyggnaden skett och att stora arealer av skärgårdens bottnar led av ansträngda syrgasförhållanden. I motsats till detta har dock regelbundna undersökningar av förekomsten av bottenlevande djur inom ramen för Stockholms stads recipientkontrollprogram givit indikationer på en påtaglig förbättring av syrgasförhållandena i Stockholms innerskärgård under det senaste decenniet.

Metodik

I föreliggande studie har vi återupprepat provtagningar av sediment i flertalet av de fjärdar i Stockholms skärgård som undersöktes under 1990-talet. Vi har jämfört de resultat som erhållits från de nya undersökningarna med resultaten från undersökningarna på 1990-talet. I innerskärgården har vi också jämfört resultaten från sedimentundersökningarna med bottenfaunaundersökningar av samma områden utifrån recipientkontrollprogrammets data. Vidare har vi i fyra utvalda områden från inner-, mellan- och ytterskärgård studerat fosfors dynamik och förekomstformer i sedimenten. Förrådet av inert och rörlig fosfor har uppskattats och storleken på sedimentation, omsättning, läckage och begravning av olika fosforformer har beräknats.

Resultat

Det är glädjande att konstatera att de resultat vi erhållit indikerar en påtaglig förbättring av syrgasförhållandena längs bottnarna i Stockholms inner- och mellanskärgård under det senaste decenniet. I flertalet av de undersökta fjärdarna var ytsedimenten oxiderade och tydliga tecken på bioturbation kunde iakttas, att jämföra mot förhållandena under 1990-talet då såväl yt- som djupsediment var laminerade och reducerade. Där det var möjligt att jämföra resultat från sedimentundersökningarna med motsvarande studier av bottenfaunans täthet och sammansättning erhölls en överväldigande samstämmighet. På de stationer där bottnarna utifrån tolkning av sedimenten klassificerades som ”döda” dvs. ytsedimenten var reducerade och laminerade var också den makroskopiska bottenfaunan utarmad. Vice versa där ytsedimenten var oxiderade och bedömdes som bioturberade insamlades också normala biomassor av evertebrater.

Vi har försökt förklara den förbättring vi registrerat i innerskärgården utifrån hypotesen att den i princip beror av en eller en kombination av följande faktorer 1) minskad tillförsel av näringsämnen från landbaserade källor, 2) minskad tillförsel av näringsämnen från utanförliggande skärgård genom vattenutbytet över Oxdjupet 3) successiv nedbrytning av historiska utsläpp som lagrats upp i sedimenten 4) en förändring av vindklimatet under det senaste decenniet resulterande i en ökad turbulens och därmed effektivare syresättning av vattnet.

För att bedöma vilka faktorer som varit betydelsefulla har vi bland annat använt oss av dynamisk massbalansmodellering för att simulera och kvantifiera vatten- och materialflödena genom innerskärgården. Våra resultat tyder på att den viktigaste faktorn bakom den observerade förbättringen är att historiskt deponerat material längs bottnarna från perioden innan modern reningsteknik infördes, genom nedbrytning, begravning och borttransport i mindre grad än tidigare påverkar förhållandena i vattenmassan. Fortfarande sker dock ett betydande läckage av näringsämnen från bottnarna, vilket förklarar den höga näringsrikedomen i innerskärgården trots att tillförseln från såväl Mälaren som reningsverken i Stockholm samt inflödet från utanförliggande skärgård minskat under senare år.

Även utanför innerskärgården har påtagliga förbättringar av bottenförhållandena noterats i ett antal fjärdar jämfört med situationen för tiotalet år sedan. Dessa områden har betydligt mindre grad jämfört med innerskärgården påverkats av tillförsel från Mälardalen. Den förbättring som vi noterat i mellanskärgården skulle därför istället kunna bero på en mer storskalig förbättring av miljöförhållandena längs svenska ostkusten. För att klarlägga den hypotesen skulle det vara önskvärt att utöka den nu genomförda studien till att också omfatta ett ytterligare antal fjärdar längs Svealands- och Östgötakusten.

Beräkning av fosforomsättning har genomförts med två alternativa metoder som gett likartade resultat. Vi kan konstatera att fosforomsättningen till stor del styrs av sedimentackumulationen. Förbättrade syrgasförhållanden i Torsbyfjärden tycks åtminstone tillfälligt ha resulterat i en ackumulation av järnbunden fosfor i ytsedimenten. Det är dock osäkert om denna fosfor fällts ut från vattenmassan eller om det funnits förutsättningar för att fastlägga dessa mängder av fosfor på väg upp från underliggande sediment.

I sedimentkärnor från Gälnan, Bullerö-, Torsby-, och Pilkobbsfjärden varierade fosfordepositionen mellan mindre än 3 och nära 5 $g \cdot m^{-2} \cdot år^{-1}$. I sedimentprofilen uppträder stabila fosforkoncentrationer redan efter mellan 2 och 10 år och mängden fosfor som årligen försvinner ur systemet beräknades till mellan 1,5 och 3 $g \cdot m^{-2} \cdot år^{-1}$. Mobil fosfor, huvudsakligen organisk och järnbunden fosfor, varierade mellan mindre än två och upp till 19 $g \cdot m^{-2}$. Beräknade läckagehastigheter till vattenmassan varierade mellan 0,2 and 2 g $P \cdot m^{-2}$. Dessa flöden bör dock betraktas som minimiflöden.

Koncentration och sammansättning av fosfor i sedimenterande material under olika säsonger och i olika miljöer skulle behöva undersökas noggrannare för att förbättra precisionen i uppskattningen av fosforomsättningen i Stockholms skärgård. Det redoxkänsliga förrådet av fosfor varierade mellan omkring 0,2 och 14 $g \cdot m^{-2}$ (en faktor 60) vilket återspeglar alternativa fördelningar av fosfor mellan sediment och vattenmassa. Extrapoleras detta till hela skärgården så innehåller ackumulationssedimenten troligen tusentals ton mobil fosfor med stor potentiell påverkan på havets vattenkvalitet.

Alla undersökta sediment förefaller vara nettosänkor för fosfor. Detta utesluter emellertid inte att sedimenten lokalt kan fungera som temporära nettokällor för fosfor, vilket indikeras av massbalanser för innerskärgården. För att kunna dra en sådan slutsats behöver dock ytterligare studier genomföras i sediment från områden med olika vattendjup och bottendynamik. Denna studie har således inte varit tillräckligt omfattande för att med säkerhet kunna fastställa skärgårdssedimentens nuvarande kvantitativa betydelse för fosfordynamiken i vattenmassan. Vi ser emellertid tydliga tecken på en positiv utveckling.

1 Part A-Laminated sediments

1.1 Introduction

Hypoxia threatens many marine ecosystems worldwide (Diaz & Rosenberg, 2008). In the Baltic Sea effects of eutrophication have for example led to oxygen deficiency with devastating effects on benthic macrofauna in many coastal areas and larger basins (Schaffner et al., 1992; Bonsdorff et al., 2002; Karlson et al., 2002; Savage et al., 2002; Kotta et al., 2007).

Rosenberg & Diaz (1993) classified the benthic habitat in the inner Stockholm archipelago in 1991 by taking sediment-surface and sediment-profile images. Surface sediments with unconsolidated soft black mud and mats of the sulfur bacteria Beggiatoa sp. (**Fig. 1-1**) predominated most of the sampling area in the water depth range between 9 and 50 m. These results suggested that the benthic habitats of the inner archipelago were threatened by poor oxygen conditions. Jonsson et al. (2003) presented results from seafloor mapping by means of side scan sonar and sediment echo sounder in combination with sediment sampling of cores from different bottom types. Most of the sampling in the inner Stockholm archipelago was undertaken between 1996 and 1998. The results from the Stockholm archipelago as a whole showed a gradually increasing portion of laminated (varved) sediments from around 1910 up to 1990, thereafter leveling off in the 1990s. The lamination is suggested to be created when macrobenthic fauna are absent or significantly reduced due to low near-bottom oxygen concentrations.

Figure 1-1 Mat of sulfur bacteria Beggiatoa sp. in surface sediment from Stockholm archipelago.

In contrast to the above described rather devastating picture of the situation along the bottoms of the inner archipelago, the City of Stockholm Environmental Monitoring Programme, applying the

Benthic Quality Index (Rosenberg et al, 2004), has shown a gradually improving status in the macrozoobenthos community since the middle of the 1990s (Lännergren et al., 2007). The trend in the time series of oxygen concentrations in near bottom waters at several sampling stations has also been increasing during recent years (see further Site description).

The aim of this study was to analyze the present benthic conditions in the inner Stockholm archipelago. The method involved analysis of sediments and macrozoobenthos from soft bottoms, comparison of these results with similar studies from the same area approximately 10 years ago and evaluation of the consistency between the sediment and benthic fauna surveys. Our hypothesis was that the signs of improved water quality during recent years seen in the city of Stockholm's environmental monitoring programme should also be reflected in the sediments.

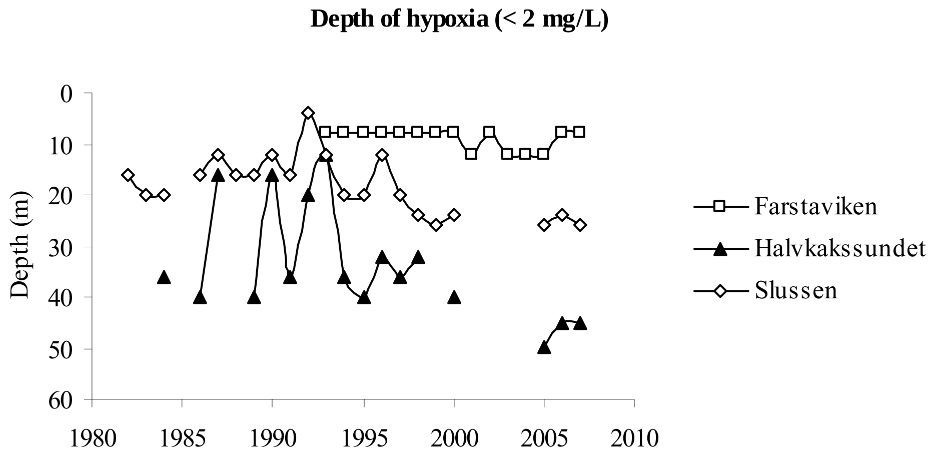
1.2 Site description and Methods

1.2.1 Background

Stockholm City is situated between Lake Mälaren to the west and the Stockholm archipelago to the east. Lake Mälaren discharges on average 164 m^3/s into the brackish water archipelago (SMHI, unpublished flow data 1961-2008, Torny Axell, pers. comm.). The inner Stockholm archipelago is an enclosed area with rocky islands surrounded by rather deep straits (30-60 m depth), and with only four narrow connections with the outer archipelago. Measurements of water quality are regularly performed by Stockholm Water (Stockholm Vatten) at a number of stations in the inner, middle and outer archipelago outside of the city of Stockholm.

The oxygen situation in stations with permanent or temporary hypoxia (O_2 concentration < 2 mg/L) is illustrated in **Figure 1-2**. The figure shows the shallowest depth below which hypoxia appeared at any time during each year. The trend after 1995 indicates an improvement of oxygen conditions (deeper depth of hypoxia) in the inner stations, most notably Halvkakssundet and Slussen. In the middle and outer stations the trend is less clear but in the outermost station Kanholmsfjärden the depth of hypoxia seems to decrease after 1995. Thus we hypothesize that oxygen conditions improved in the inner archipelago but worsened in the open sea exemplified by Kanholmsfjärden after 1995.

a)



b)

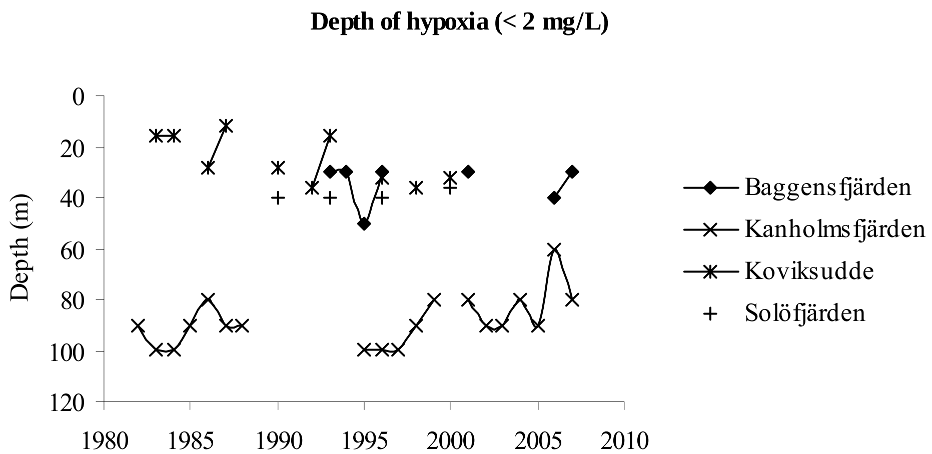


Figure 1-2 Depth of hypoxia (yearly oxygen minimum < 2 mg/L) in a) inner stations and b) middle and outer stations. Data from Stockholm Water database

In relation to the apparent changes in oxygen conditions we now examine the corresponding trends in water quality. In **Figure 1-3** the deep water salinity at inner stations is shown. There seems to be a decreasing trend which might reflect a greater proportion of fresh water possibly connected to runoff and hence a decreasing sea water contribution. There is no similar trend seen in the deep water salinity in the middle and outer stations.

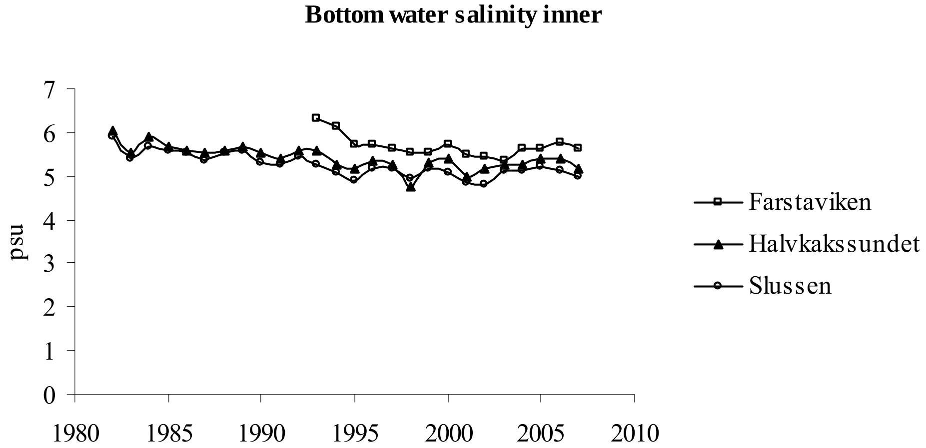
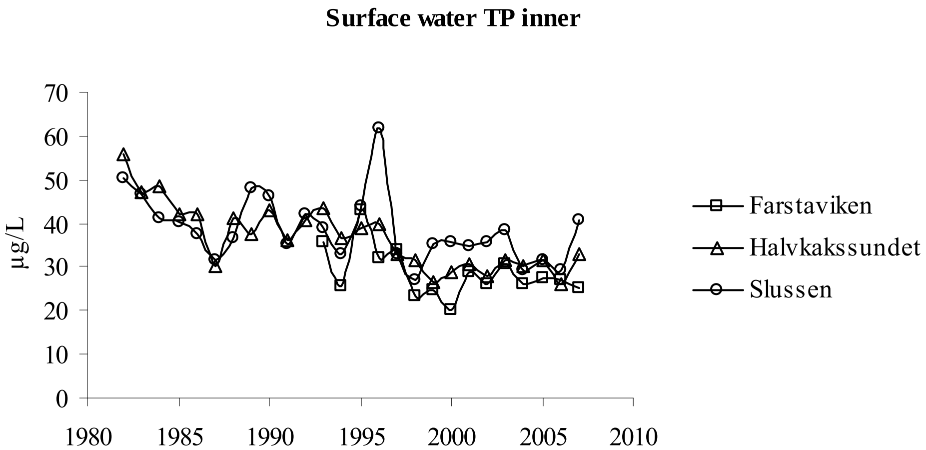


Figure 1-3 Bottom water salinity in inner stations. Data from Stockholm Water database.

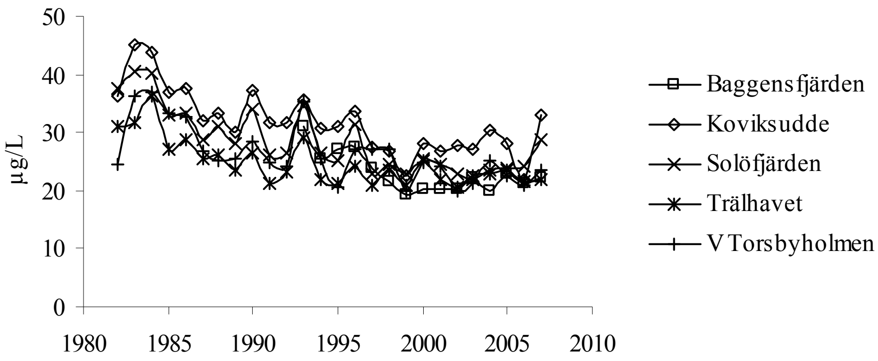
Total phosphorus concentrations in surface water are shown in **Figures 1-4a-c**. There seem to be decreasing trends for surface water concentrations at least in inner and middle stations, which are likely to be linked to a decreasing external load. The deep water concentrations are generally more variable and it is difficult to detect any temporal trends. In **Figure 1-4d** the deep water total phosphorus concentrations in the outer stations are shown. There seems to be a partial relationship between hypoxia (**Fig. 1-2b**) and the deep water total phosphorus concentration in Kanholmsfjärden.

a)



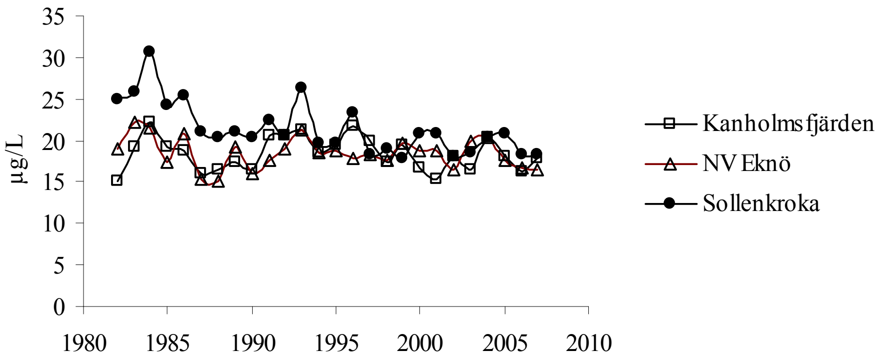
b)

Surface water TP middle



c)

Surface water TP outer



d)

Bottom water TP outer

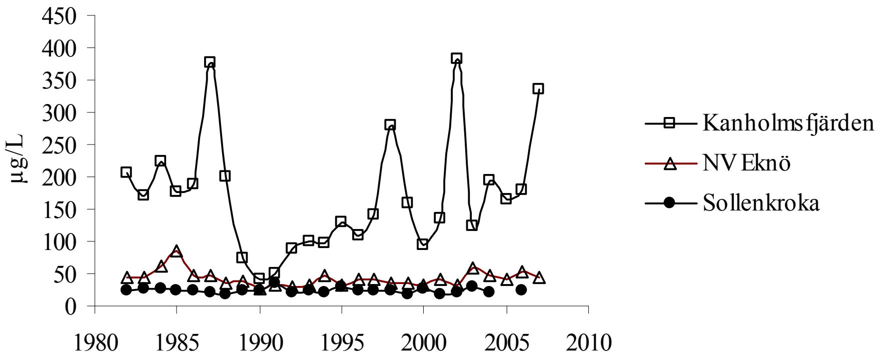
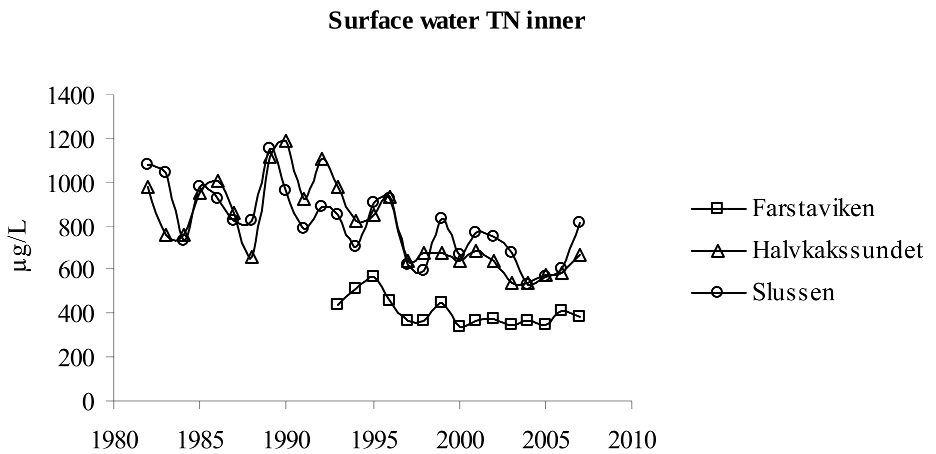


Figure 1-4 Total phosphorus concentrations in surface water for a) inner stations; b) middle stations; c) outer stations; and in deep water for d) outer stations. Data from Stockholm Water database.

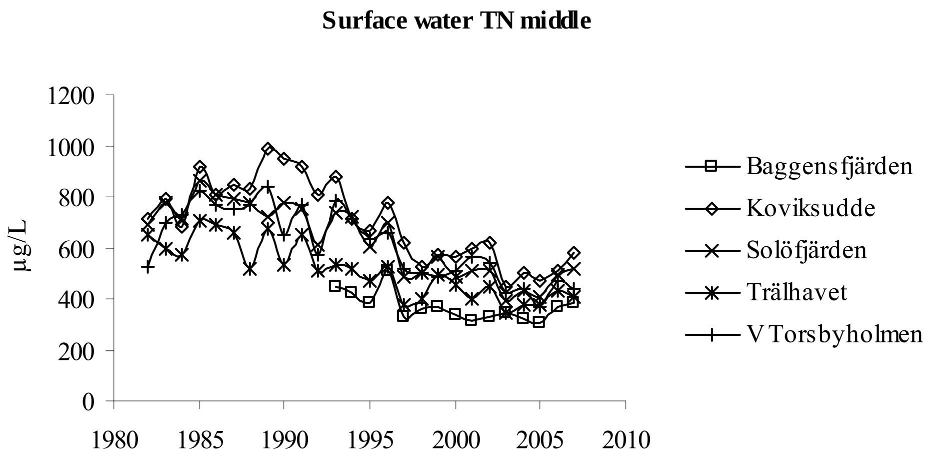
Surface water trends for nitrogen resemble phosphorus trends as seen in **Figure 1-5a-c**, but the decrease is indeed more pronounced in the inner and middle archipelago. More dramatic shifts are seen in ammonium concentrations in some inner and middle stations after 1995 (**Fig. 1-6a, b**). In

Figures 1-6d-f deep water ammonium concentrations are shown and it is apparent that ammonium release from sediments happened occasionally in Farstaviken, Baggensfjärden and Kanholmsfjärden, likely due to anoxia.

a)



b)



c)

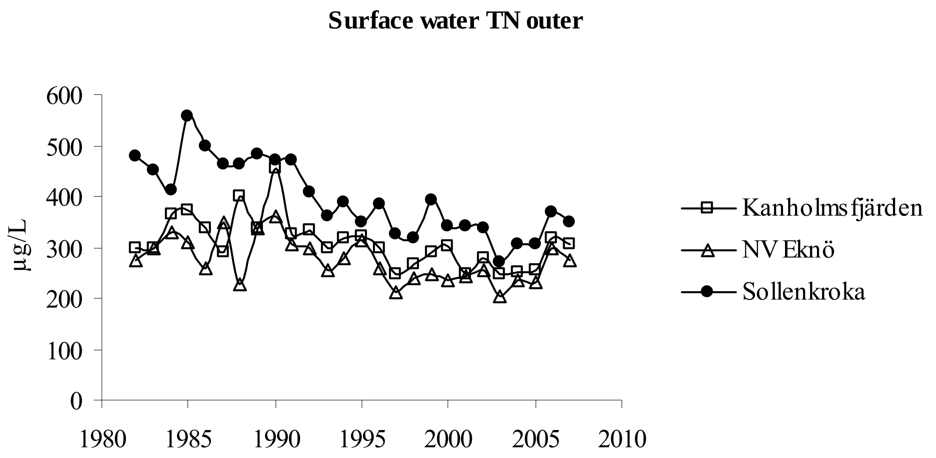
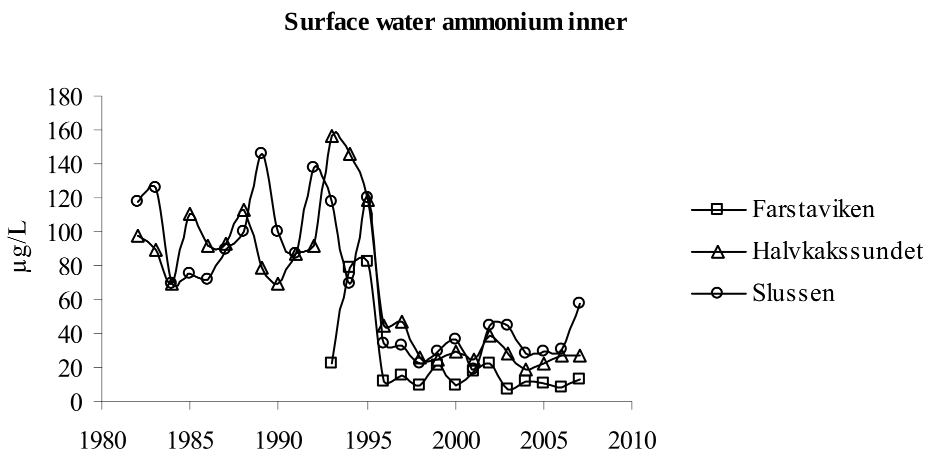
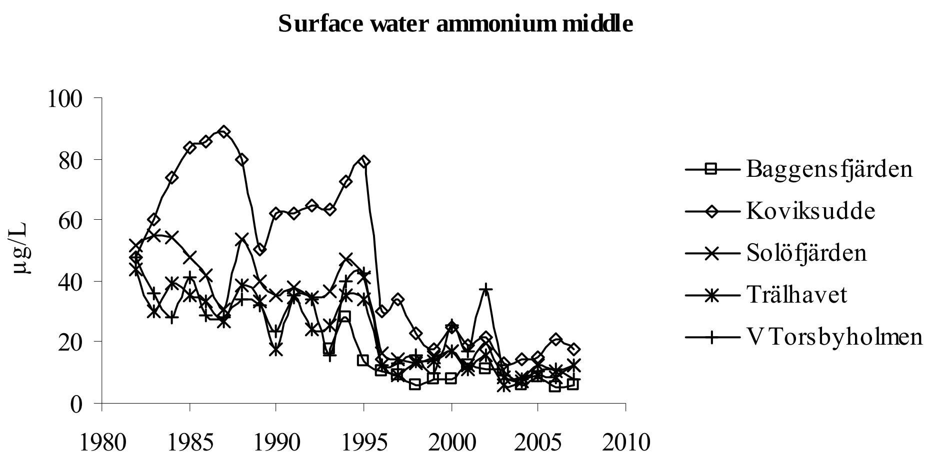


Figure 1-5 Total nitrogen concentrations in surface water for a) inner stations; b) middle stations; c) outer station. Data from Stockholm Water database.

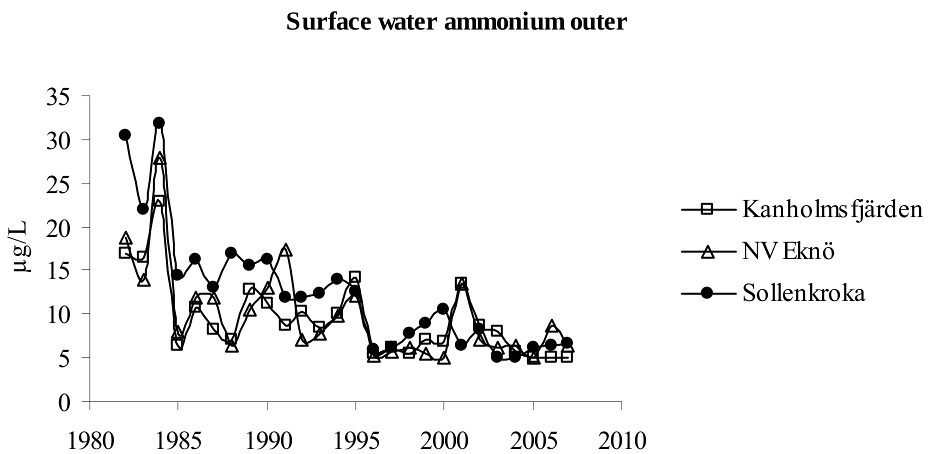
a)



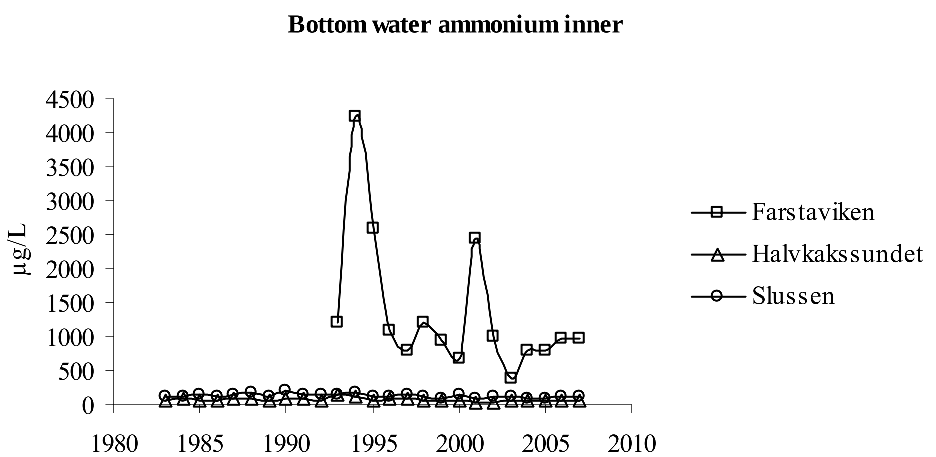
b)


Surface water ammonium middle
100
80
60
40
20
0
µg/L
1980
1985
1990
1995
2000
2005
2010
Baggensfjärden
Koviksudde
Solöfjärden
Trälhavet
V Torsbyholmen

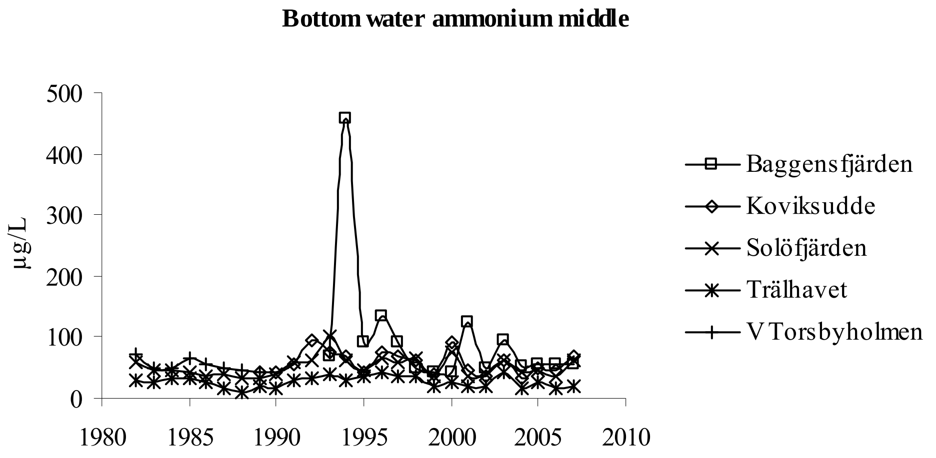
c)


Surface water ammonium outer
35
30
25
20
15
10
5
0
µg/L
1980
1985
1990
1995
2000
2005
2010
Kanholmsfjärden
NV Eknö
Sollenkroka

d)


Bottom water ammonium inner
4500
4000
3500
3000
2500
2000
1500
1000
500
0
µg/L
1980
1985
1990
1995
2000
2005
2010
Farstaviken
Halvkakssundet
Slussen

e)



f)

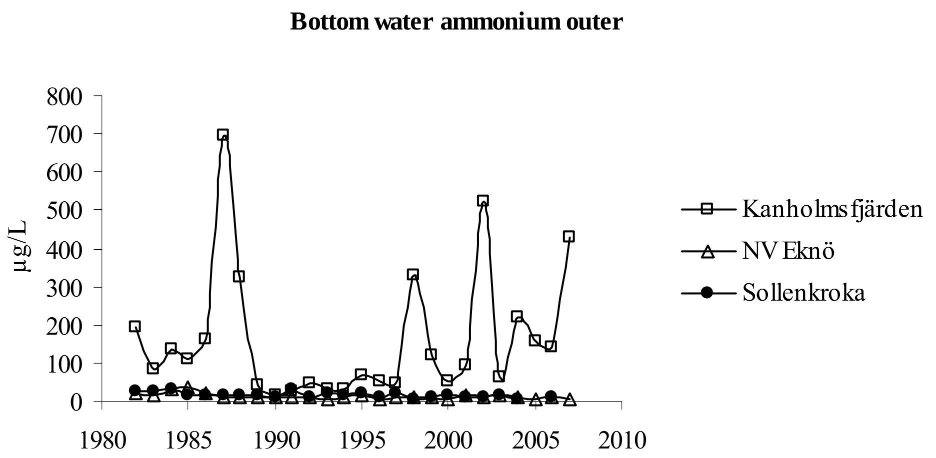
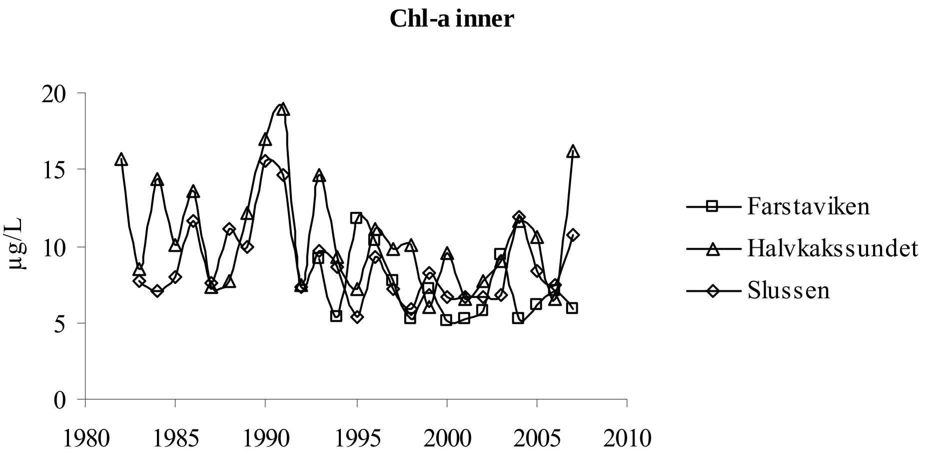


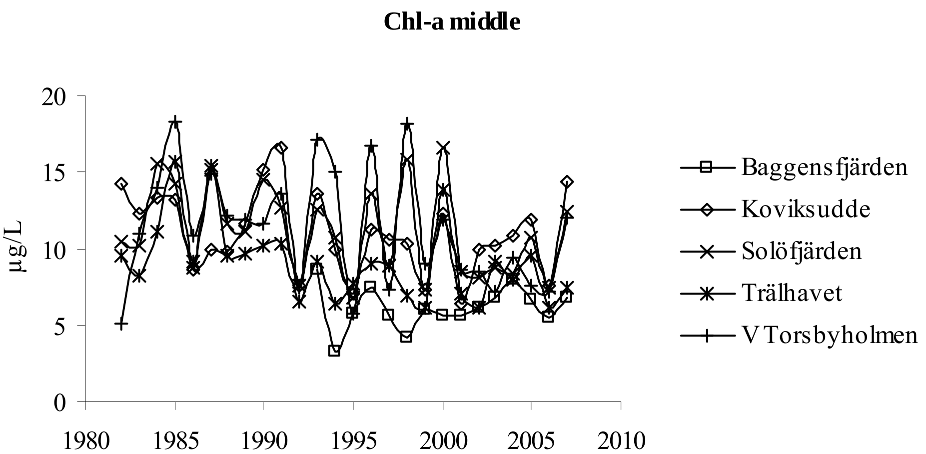
Figure 1-6 Ammonium concentrations in surface water for a) inner stations; b) middle stations; c) outer stations; and in deep water for d) inner stations; e) middle stations; f) outer stations.

In **Figure 1-7** the historical development of chlorophyll-a concentrations is shown for different stations. It is not easy to detect any clear trends for annual mean values. The same is true for measurements in August. However, there seems to be a slight increase in August concentrations of chlorophyll-a in the outer stations which could possibly be due to cyanobacteria favoured by decreasing nitrogen concentrations. In **Figure 1-8** annual mean values of Secchi depth are shown. Apparently there is an improvement in the Secchi depth during the period, at least in the inner and middle stations.a)

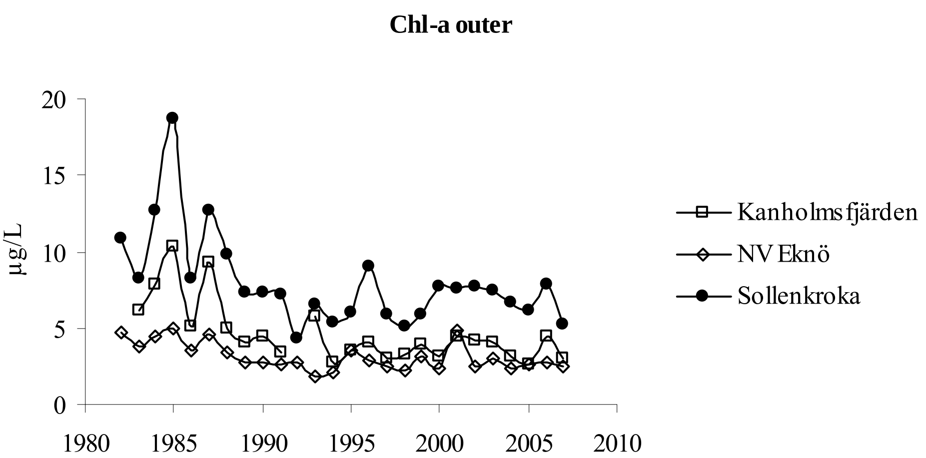
a)


Chl-a inner
µg/L
20
15
10
5
0
1980
1985
1990
1995
2000
2005
2010
Farstaviken
Halvkakssundet
Slussen

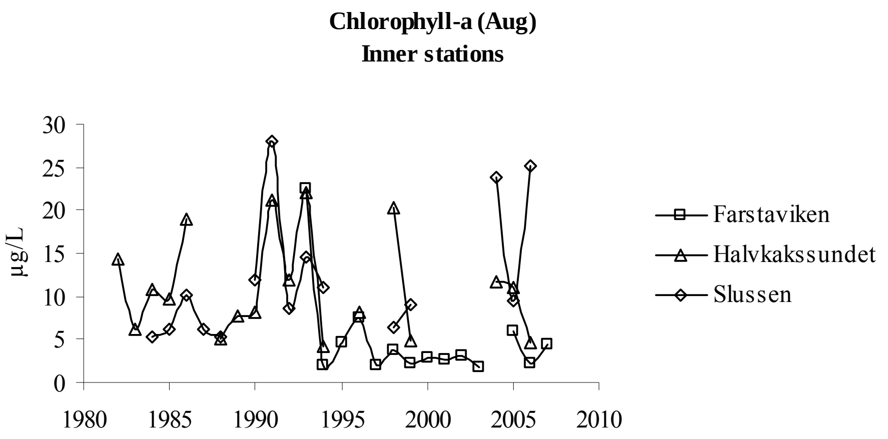
b)


Chl-a middle
µg/L
20
15
10
5
0
1980
1985
1990
1995
2000
2005
2010
Baggensfjärden
Koviksudde
Solöfjärden
Trälhavet
V Torsbyholmen

c)


Chl-a outer
µg/L
20
15
10
5
0
1980
1985
1990
1995
2000
2005
2010
Kanholmsfjärden
NV Eknö
Sollenkroka

d)



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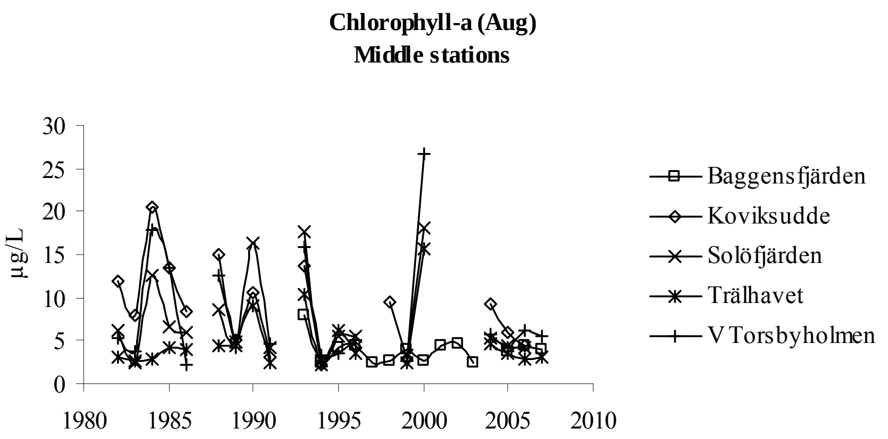


f)

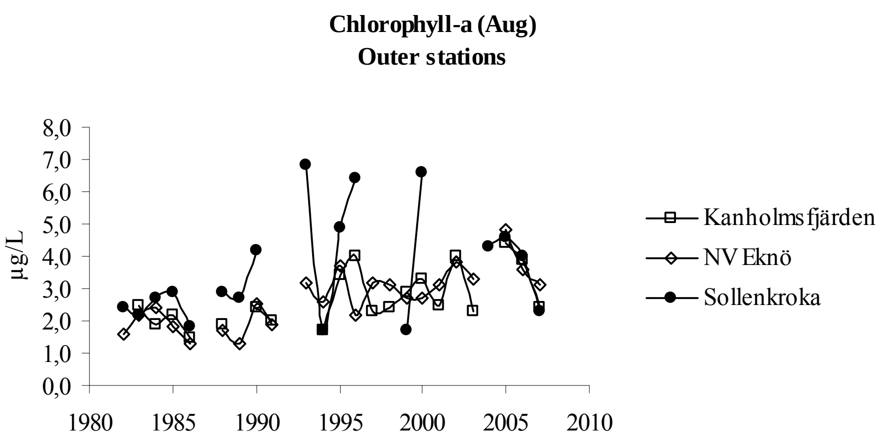
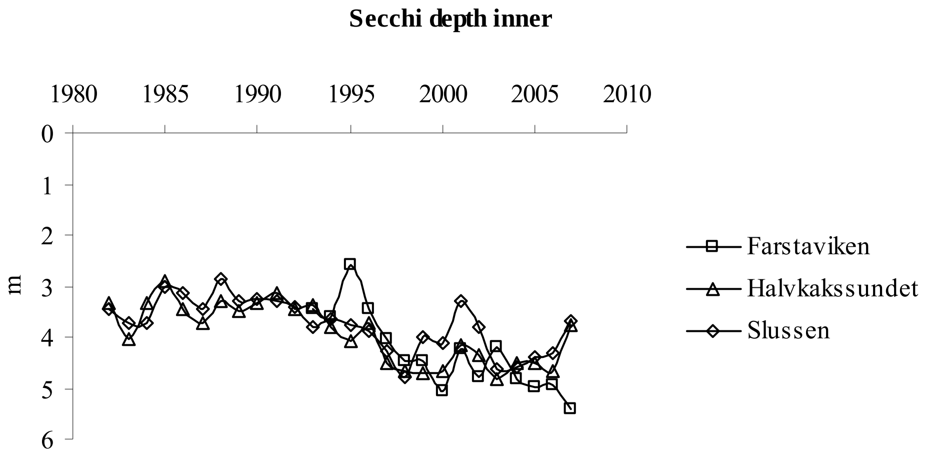
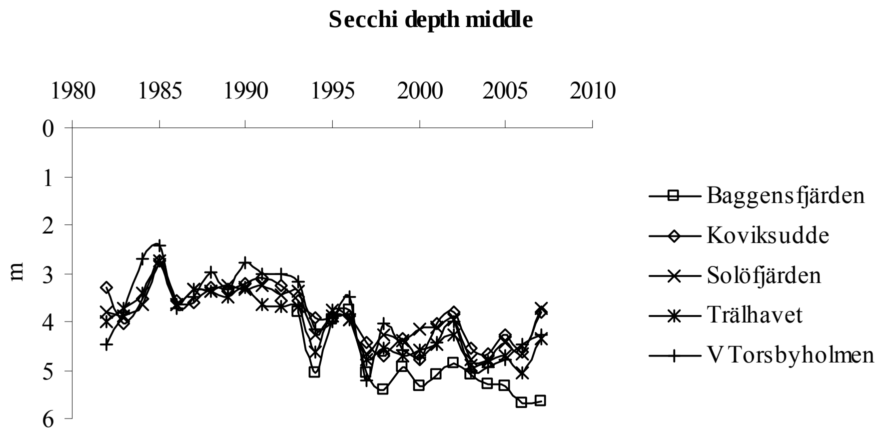


Figure 1-7 Chlorophyll-a concentrations annual mean values in a) inner stations; b) middle stationsand c) outer stations; August values for d) inner stations; e) middle stations and f) outer stations. Data from Stockholm Water database

a)



b)



c)

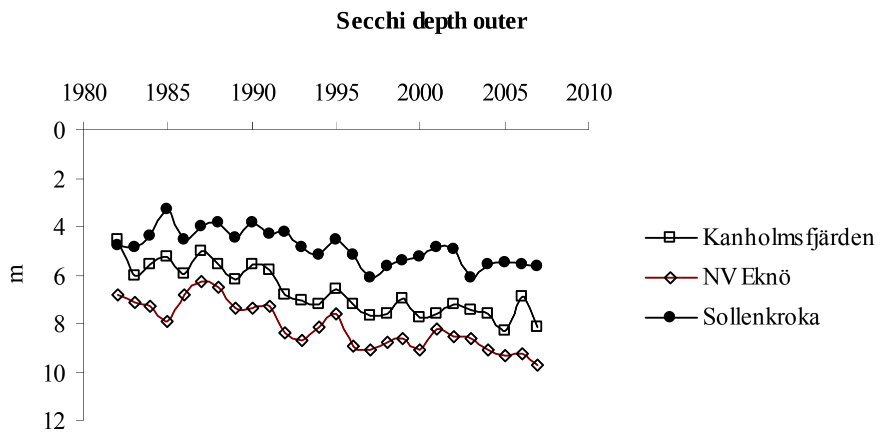


Figure 1-8 Annual mean values of Secchi depth in a) inner stations; b) middle stations; c) outer stations. Data from Stockholm Water database.

In **Figure 1-9** we show a regression between total phosphorus (TP) concentrations and Chlorophyll-a concentrations (averages July to September) in surface waters of 17 Scandinavian coastal waters, stretching from Northern Bothnian to southern Baltic proper. As seen from the figure, the inner archipelago site has the highest recorded Chl-a and TP concentrations of all the studied areas. It is also worth noting that the inner archipelago deviates from the regression trend line, having higher Chl-a levels than expected. A possible explanation could be that the inner archipelago, in common with the other areas with the strongest deviation upwards (Bråviken-Motala ström, Skutskärsfjärden-Dalälven and Yttrefjärden-Pite älv), is an estuary. Salinity is lower in estuaries, which favours algae blooming in late summer. In addition, estuaries are also known as typically high productive areas. There is a general formula addressing how salinity influences the Chl-a/TP ratio in coastal ecosystems (Håkanson & Bryhn, 2008). However, using this formula did not increase the r^2-value in the regression in **Figure 1-9** indicating there are also other factors behind the high Chl-a levels in the inner archipelago.

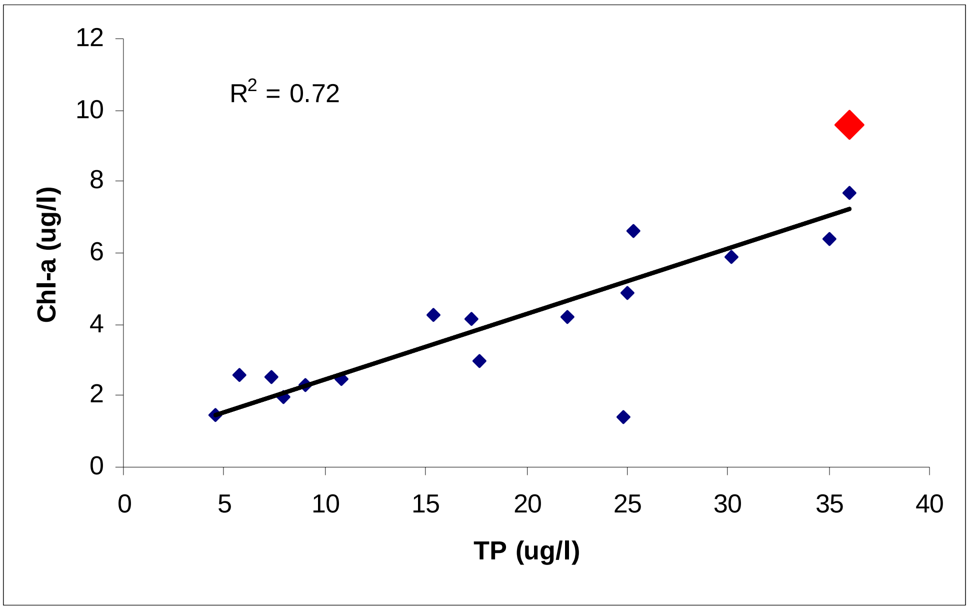


Figure 1-9 A regression between total phosphorus (TP) concentrations and Chlorophyll-a concentrations(averages July to September) in surface waters of 17 Scandinavian coastalwaters, stretching from Northern Bothnian bay to southern Baltic proper including inner Stockholm archipelago (red large dot). Modified from Malmaeus et al. (2008).

One likely effect of the improved oxygen conditions in the bottom waters of the archipelago is a reduced phosphorus leakage from reduced sediments. As an illustration, the oxygen saturation and the phosphate concentration at 40 meter depth in Halvkakssundet is shown in **Figure 1-10**. The oxygen minima generally appearing in autumn indicate improved oxygen conditions following the mid-90s. This improvement happens together with lower phosphate levels corresponding with the oxygen minima. The yearly phosphate peaks in deep waters are thus probably explained by leakage from reduced sediments due to anoxia.

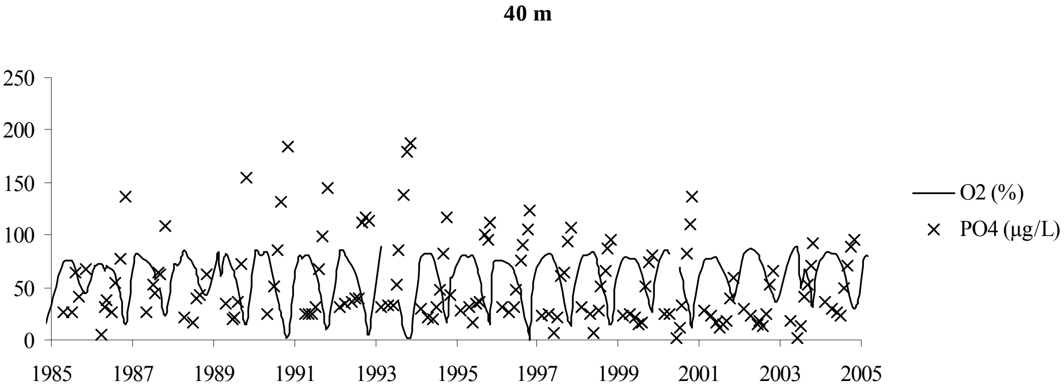


Figure 1-10 Oxygen saturation and phosphate concentration at 40 m depth in Halvkakssundet between 1985 and 2005. Data from Stockholm Water database.

1.2.2 Methods

Sampling

In this study sediment samples were taken from 2-3 stations at a series of 21 coastal areas (**Fig. 1-11**). A majority of the stations in the inner archipelago are part of the Environmental Monitoring Programme of the City of Stockholm and macrozoobenthos have been monitored every other year since 1968. Sediment sampling has also been conducted widely in the area during various excursions in the second half of the 1990s, which have been reported in Jonsson et al. (2003). We compared the results from the present sediment survey with the monitoring of zoobenthos that was undertaken in May-June 2008. We also compared present results with equivalent sampling excursions in the late 1990s.

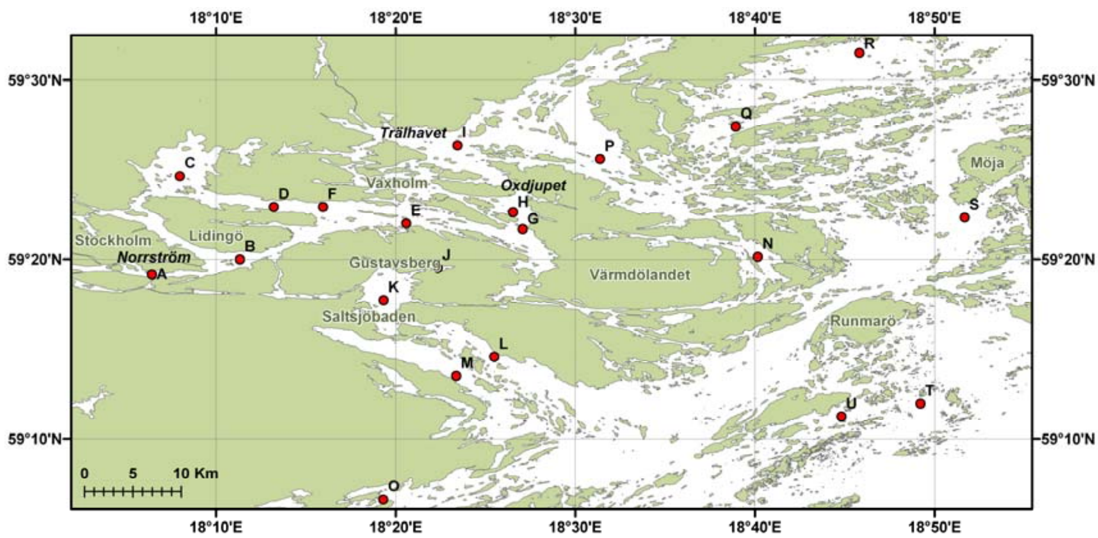


Figure 1-11 Map of the study area in the Stockholm archipelago with sub-areas (A-U) marked.

Sediment sampling was conducted in June, September, November and December 2008. Sediment samples were taken with a Gemini double corer (inner diameter 80 mm), which allows free water passage through the sample during descent and sediment penetration (**Fig. 1-12**). The core was only accepted if the sediment surface was intact. All sampled cores were stored at 4° C until preparation in the laboratory. Before cutting the cores into two longitudinal halves, exposing the vertical structures, each core was put in a freezer for approximately two hours to minimize disturbance of the very loose surficial sediments. This stabilized the outer 2-5 mm of the sediment column, leaving the central parts unfrozen and structures preserved. The section surfaces were examined described and photographed (digital format, 4 mega pixels), and the lamination patterns were recorded. The examination protocols and the photographs of the sediment cores were compared with similar descriptions of sediment cores in the same area from the 1990s.

Figure 1-12 The Gemini core sampler ready to be launched from Research Vessel Perca.

Statistics

To test whether any statistically significant change in the occurrence of reduced surface sediments or benthic fauna took place between the late 1990s and the present survey we assumed that the samples are matched-pairs following the binominal distribution. A null hypothesis was formulated:

H_0: $p=0.5$ was tested against H_1: $p > 0.5$

Having formulated the null hypothesis the level of significance for the probability of error was calculated.

To estimate how large the differences between the samples from respective decades were we approximated the prevailing binominal distribution with a normal distribution making it possible to calculate approximate confidence intervals through:

$$\frac{n_{1+}-n_{+1}}{n_{++}} \pm 1.96 \frac{\sqrt{n_{12}+n_{21}+1-\left(n_{12}-n_{21}\right)^2 / n_{++}}}{n_{++}} \tag{1}$$

We also used a contingency table (Helsel & Hirsch, 2002) to test the same changes mentioned above. The null hypothesis for this test was formulated:

H_0: = No changes was tested against H_1: Change of occurrence

The benthic fauna was tested against the χ^2 distribution with 1 degree of freedom.
For the reduced surface sediments the test was performed with the Fisher's Exact Test distribution with 1 degree of freedom since the criteria for using the χ^2 distribution was not fulfilled (too few observations).

As the number of observations in this study is small the estimated performance measures are associated with a great deal of uncertainty. To account for this we also calculated Bayesian confidence intervals (Jaynes, 1976), rather than point estimates. The accuracy and specificity of the tests are reported as shortest confidence intervals (Nicholson, 1985), under the assumption that all values are equally probable. The calculations were performed using an online calculator on (http://www.causascientia.org/math stat/ProportionCI.html, Jan 23, 2009). The values reported defines the boundaries of an interval that, with certain certainty, contains the true value of the accuracy, sensitivity or specificity.

Model setup

To put the results from the surveys of the seabed into perspective we established simple mass balance models for the turnover of total phosphorus, total nitrogen and ammonia in the inner archipelago. To solve the system of first order, ordinary differential equations which describe input, output and retention of the actual substances the software tool Stella® was used. In the case of total phosphorus a higher resolution model described in Malmaeus et al., (2008) was also used. The prerequisites for our modelling efforts are summarized in **Table 1-1**. Morphometrical characteristics were calculated from data presented in SMHI (2003) and Jonsson et al. (2003). Flow data for Lake Mälaren outflow through River Norrström was provided by SMHI (Torny Axell, pers. comm.) The inflow of water from the outer archipelago goes mainly (around 85 %) through the sound Oxdjupet (**Fig. 1-11**), but also through the sounds; Kodjupet, Stegesund, Skävsjöholmssundet and Baggen-Stäket. The sum of water flows into the area was calculated through simple mass balance calculations for salt, applying Knudsen's relations (Knudsen, 1900). The idea is to calculate how large the inflow of saline rich water from the outer archipelago must be to maintain the measured salinity in the inner archipelago given the flow of fresh water from Lake Mälaren (**Fig. 1-13**). Using long term data on salinity from Stockholm Water database it was possible to calculate the average inflow to approximately 325 m^3/s. This order of magnitude is close to what Engqvist & Andrejev (2003) found using a fine resolution hydro dynamical model to calculate the water exchange in Stockholm archipelago for the year 1992. The inflow in that year was calculated to average around 390 m^3/s (Engqvist & Andrejev, 2003). Nutrient concentrations and transports in River Norrström are monitored in the Swedish national Environmental Monitoring Programme and are records are kept by the Department of Aquatic Science and Assessment, Swedish University of Agricultural Sciences (www.ma.slu.se). Nutrients concentrations in the inner archipelago, Trälhavet (the basin outside Oxdjupet, **Fig. 1-11**) and the discharges from city of Stockholm's sewage treatment plants (STPs) was provided through Stockholm Water database (Christer Lännergren, pers. comm.). The sill depth in Oxdjupet is 20 m.

Lännergren et al., (2007) showed that the inflowing water from Trälhavet through Oxdjupet in most situations originates from 20-30 m depth, with some variation. In this study the inflowing water quality was approximated by averaging water characteristics from the water column in Trälhavet between 10 and 40 m.

The sediment characteristics were calculated from data collected in this study (presented in part B). Of the more important fluxes, phosphorus leakage from sediments is the most difficult to assess, mainly due to the fact that reliable measurements are missing. Modellers often treat sediments like a "black box" used to explain variations in the water mass that cannot be explained by monitored fluxes. The model used here includes algorithms for leakage based on sedimentation, temperature and oxygen concentration but the leakage rate has been scaled (calibrated) to fit empirical data on phosphorus concentration in the water column. An outline of the model for total phosphorus is presented in **Figure 1-14**.

Table 1-1 A compilation of environmental characteristics of the inner Stockholm archipelago calculated as averages for the periods 1982-1995 and 1996-2007 respectively.

Parameter	1982-1995	1996-2007
Morphometry		
Area (km^2)	108.6	
Average depth (m)	13	
Maximum depth (m)*	57	
Volume (km^3)	1,45	
Proportion of accumulation areas (%)**	44	
Water Flows		
Norrström (m^3/s)****	173	164
Inflow from the sea (m^3/s)	325	325
Nutrient concentrations		
Norrström (C_{in}) Tot-P (µg/l)****	38	29
Norrström (C_{in}) Tot-N (µg/l)****	670	660
Norrström (C_{in}) NH_4-N (µg/l)****	55	19
Trälhavet mean 10-40 m (C_{sea}) Tot-P (µg/l)*****	26	24
Trälhavet mean 10-40 m (C_{sea}) Tot-N (µg/l)*****	380	300
Trälhavet mean 10-40 m (C_{sea}) NH_4-N (µg/l)*****	27	17
Inner archipelago mean 0-15 m Tot-P (µg/l)*****	44	38
Inner archipelago mean 0-15 m Tot-N (µg/l)*****	930	630
Inner archipelago mean 0-15 m NH_4-N (µg/l)*****	140	72
Nutrient transports		
Norrström Tot-P (tonnes/yr)****	180	150
Norrström Tot-N (tonnes/yr)****	4 200	3 500
Norrström NH_4-N (tonnes/yr)****	290	70
Trälhavet Tot-P (tonnes/yr)	270	250
Trälhavet Tot-N (tonnes/yr)	3 900	3 100
Trälhavet NH_4-N (tonnes/yr)	280	170
STP discharge Tot-P (tonnes/yr)*****	60	30
STP discharge Tot-N (tonnes yr/)*****	4 100	1 800
STP discharge NH_4-N (tonnes/yr)*****	2 200	460
Other water characteristics		
Trälhavet mean 10-40 m salinity (PSU)*****	5.8	5.4
Inner archipelago mean 0-15 m salinity (PSU)*****	3.3	3.2
Inner archipelago mean 20-50 m salinity (PSU)*****	5.5	5.1
Inner archipelago mean 20-50 m O_2 (mg/l)*****	7.4	7.4
Inner archipelago chlorophyll-a (µg/l)*****	11.4	9.9
Inner archipelago Secchi depth (m)*****	3.4	4.2
Sediment characteristics		
Sediment water content (%)		88
Sediment organic content (%)		15
Sediment Tot-P concentration (mg/kg TS)		4.2

* SMHI (2003), ** Jonsson et al. (2003) ***unpublished data from SMHI; ****data from Department of Aquatic Science and Assessment, Swedish University of Agricultural Sciences; *****Stockholm Water database

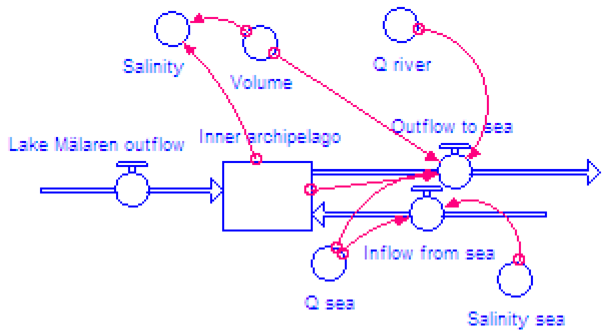


Figure 1-13 Principal illustration of the mass balance for salt in an estuary also recognized as Knudsen's relations (Knudsen, 1900).

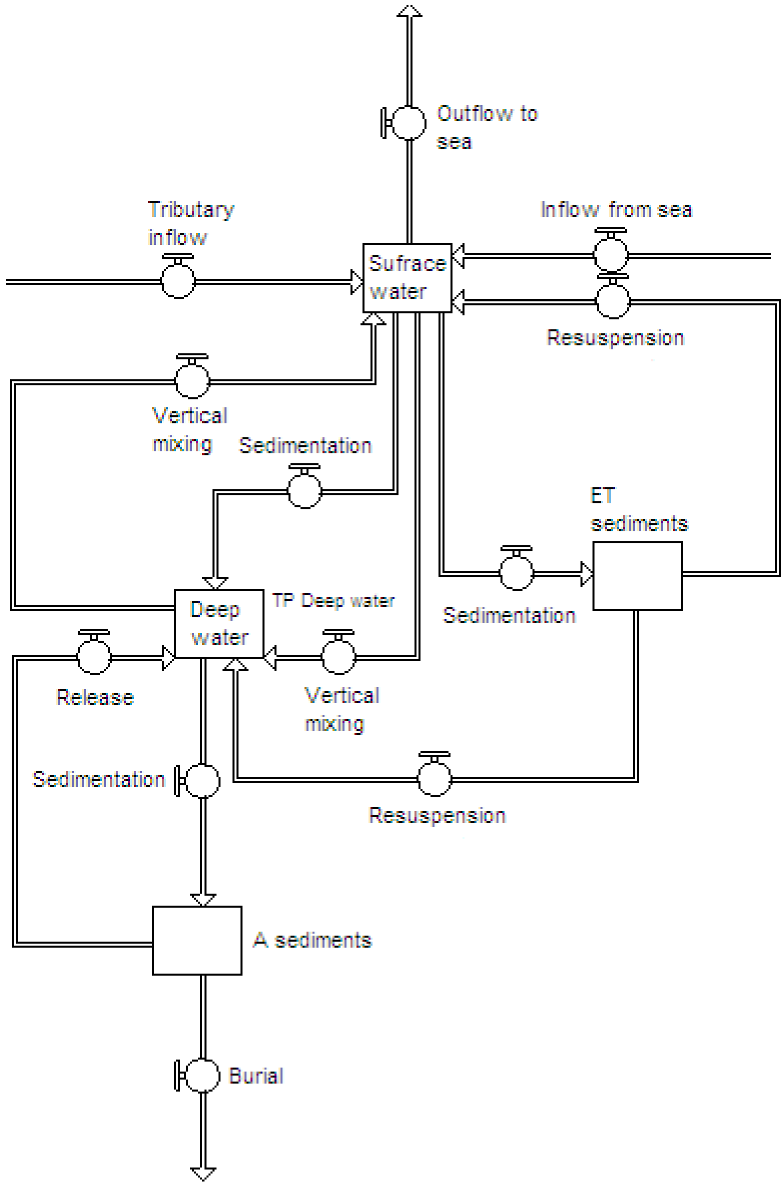


Figure 1-14 Outline of the model for total phosphorus turnover. Modified from Malmaeus et al. (2008).

1.3 Results

1.3.1 Sediment survey

Inner archipelago

Torsbyfjärden / Solöfjärden sub-area G / H

Significant changes were detected in the deepest parts of Torsbyfjärden Bay (**Fig. 1-15**) situated in the northern part of the bay. In 1996, the entire sediment core was reduced all the way up to the surface sediment, showing clear lamination from the bottom of the core up to around 20 cm from the surface (**Fig. 1-16**). Above this, the sediment surface diffusely laminated sediment was found in 1996. In 2008 however, the upper 5-6 cm at a water depth of 50 m showed oxidised sediment without structure clearly indicating bioturbation. In 2008 the sediment was also bioturbated in shallower areas at water depths of 40 m (**Fig. 1-17**) showing a thickness of the bioturbated layer of 7-9 cm. In 1996, the oxygen conditions were much worse in these bottom areas showing dark, reduced and laminated sediments even in the surficial sediment. During a PhD course in 1998 (Anon. 1998) a depth gradient was studied to find out the upper depth limit of lamination at the sites 1 (34 m), 2 (10 m), 3 (12 m) and 4 (15 m) in the southern parts of Torsbyfjärden Bay (**Fig. 1-15**). The core from 12 m was bioturbated in the upper part from approximately 1985, whereas below this level clear lamination was found from the mid 1940s up to 1985. At 15 m (stn. 4) clear lamination was found all through the core up to the sediment surface (**Fig. 1-17**). Obviously the limit between lamination and bioturbation occurred between 12 and 15 m in 1998. However, the situation was even worse in the early 1980s.

Jonsson et al. (1990) found a weak correlation (r^2=0.3) between increasing water depth and number of annual varves indicating that the low oxygen concentrations occur first in the deep water turning the sediment structure from bioturbated into laminated. Inversely, when improved oxygen conditions occur it is likely to first occur in the more shallow parts and later at larger depths. Such a relationship is supported by the conclusion mentioned above. At present the upper sediments are bioturbated in the entire bay. Based on measuring the lamina thicknesses (average 1.3 cm) in the cores from 40 and 50 m at 11-16 cm and 12-22 cm (**Fig. 1-16** and **1-17**) and assuming that the deposition rate in the upper unconsolidated and bioturbated layer is 1.5 times higher (i.e. 2 cm yr^{-1}) than in the deeper and more consolidated laminated parts we can estimate the turnover from laminated to bioturbated sediments to have occurred during the last few years in the deep parts of the bay. Taking into account a significant bioturbation of soft-bottom macro fauna in the Baltic Proper of approximately 1.5-2 cm and that this may indicate an earlier recovery of the benthic system depending on how large the annual deposition is, we can conclude that oxygen conditions improved substantially in 2005 at 40 m and 2006 at 50 m. In the adjacent Solöfjärden Bay similar conditions were observed.

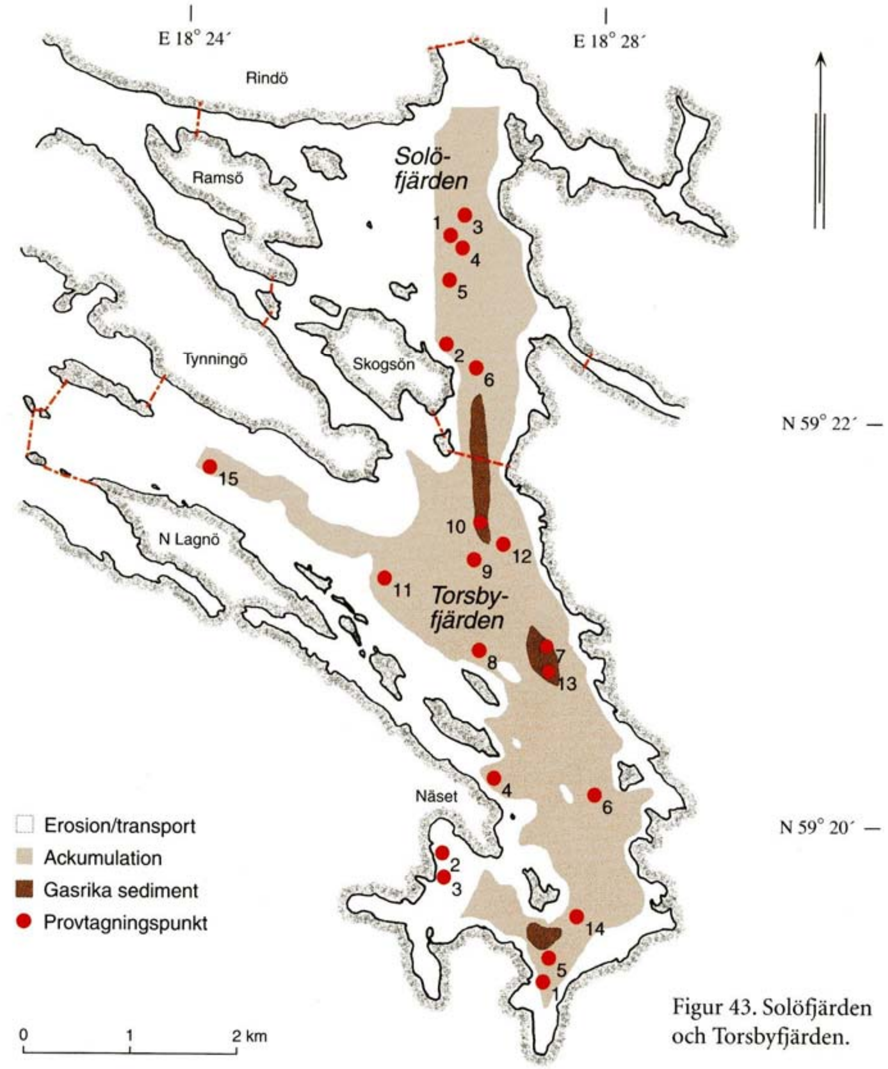


Figure 1-15 Bottom dynamic map of Solöfjärden and Torsbyfjärden. From Jonsson et al. (2003).

Figure 1-16 Photographs of sediment cores from Bay Torsbyfjärden from left to right 1/ 2008 depth 50 m, 2/ 1996 depth 46.5 m.

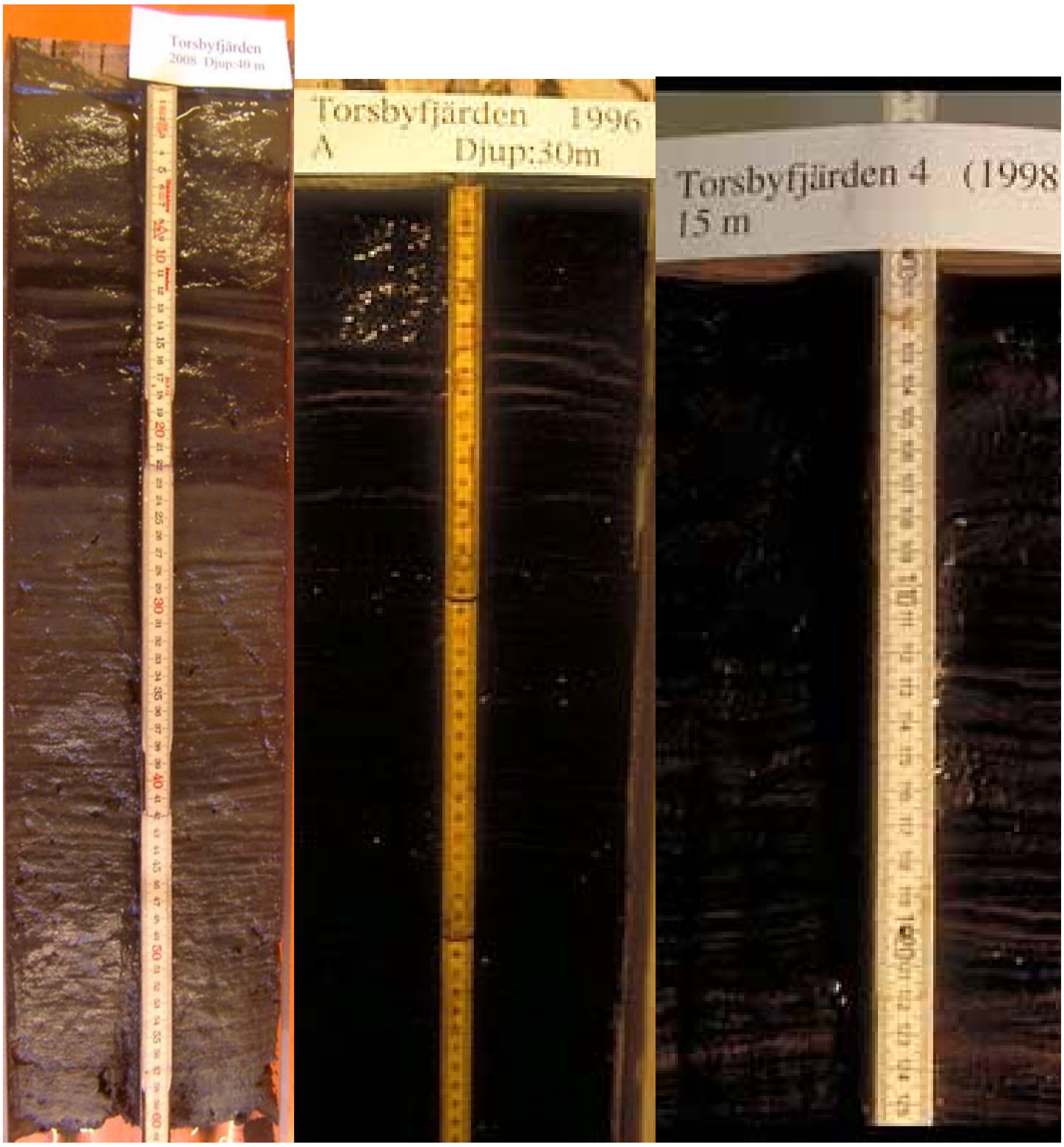


Figure 1-17 Photographs of sediment cores from Bay Torsbyfjärden from left to right 1/ 2008 depth 40 m, 2/ 1996 depth 30 m, 3/ 1998 depth 15 m.

Baggensfjärden sub area K

In Baggensfjärden Bay clear improvements have occurred between the mid 1990s and 2008. However, in the deepest parts anoxic and laminated sediments still occur which are shown in the core sampled from 50 m water depth (**Fig. 1-18**). In 1996 dark laminated sediments were also found in the upper parts of the core. At 40 m a bioturbated layer of 6-7 cm overlays a clearly laminated layer. A similar pattern occurs also at 28 m (**Fig. 1-19**) with approximately 5-6 cm bioturbated sediments on top of a laminated layer. In a core from 1998 (Anon., 1998), however, the lamination goes all the way to the top of the core and the sediment is black and reduced. This is also the case in a core from 1998 sampled at 18 m.

Using the same presumptions for the calculations as for Torsbyfjärden concerning bioturbation depth, the improved oxygen conditions occurred around 2004 both at 28 and 40 m water depth.

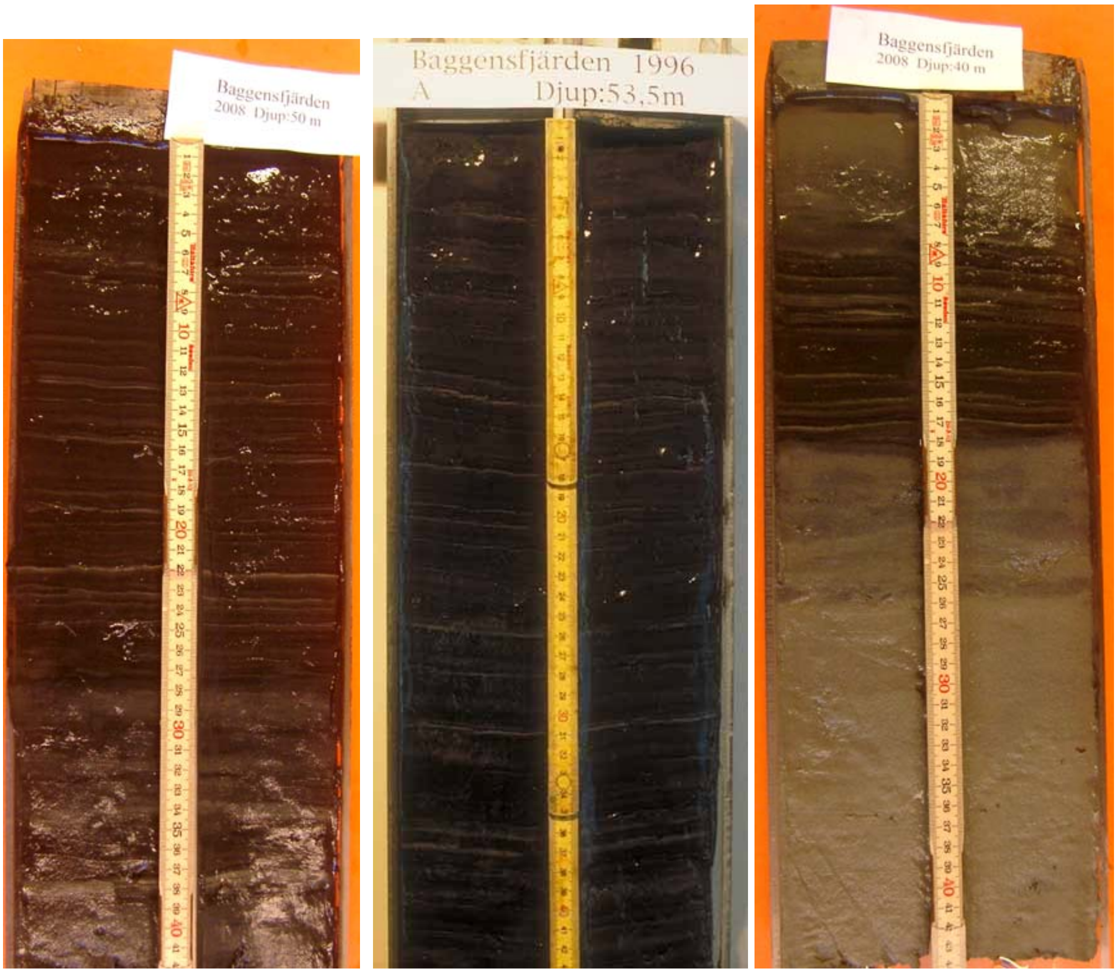


Figure 1-18 Photographs of sediment cores from Bay Baggensfjärden from left to right 1/ 2008 depth 50 m,2/ 1996 depth 53,5 m, 3/ 2008 depth 40 m.

Figure 1-19 Photographs of sediment cores from Bay Baggensfjärden from left to right 1/ 2008 depth 28 m, 2/ 1998 depth 27 m, 3/ 1998 depth 18 m.

Middle archipelago

Östra Saxarfjärden / Trälhavet sub-area P / I

The sediments in the Östra Saxarfjärden Bay are in general difficult to interpret. The lamination is often diffuse and clear lamination often alternates with thick black reduced layers that not correspond to annual lamination (Jonsson unpublished material and Anon., 1993). All sediment cores taken from less than 50 m in September 1994 had an oxidized upper layer (Anon. 1994). A comparison between cores taken in 2008 and 1996 (**Fig. 1-20**) confirms that the interpretation is difficult and that sediment diagenetic processes govern the sediment structure rather than the annual sedimentation cycle.

The situation in Trälhavet is also quite problematic to interpret which was stated already in the investigation in 1992 (Anon., 1992). The core stratigraphy which is displayed in **Figure 1-21** supports this conclusion. The upper 5-6 cm of the sediment column is oxidised and probably bioturbated, which might be an indication of improving bottom conditions.

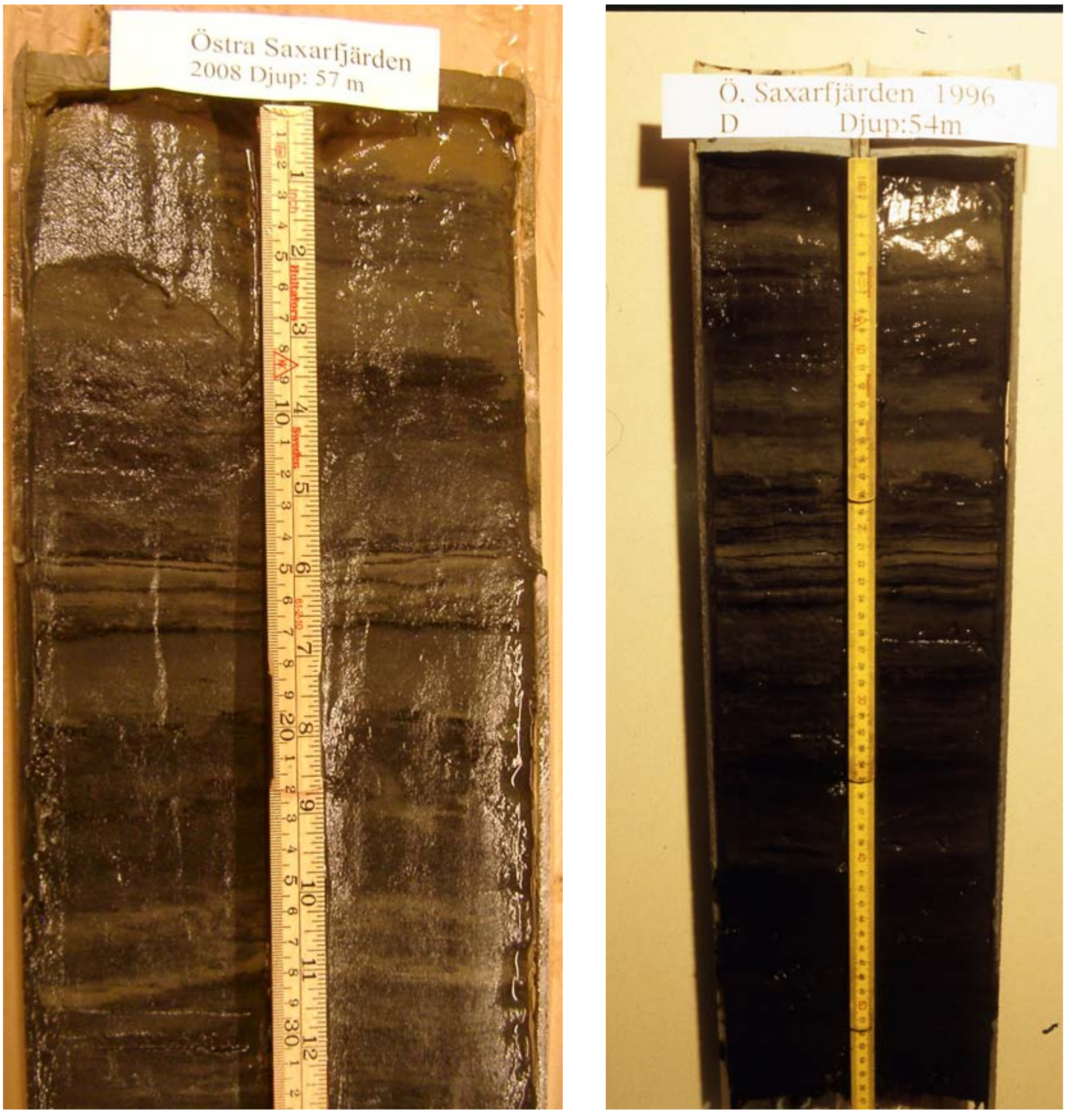


Figure 1-20 Photographs of sediment cores from Bay Östra Saxarfjärden from left to right 1/ 2008 depth 57 m, 2/ 1996 depth 54 m.

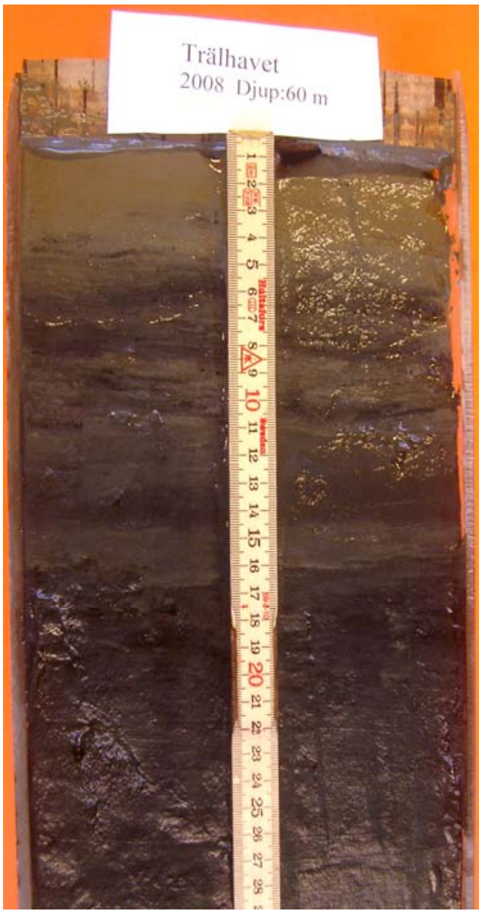


Figure 1-21 A sediment core from Bay Trälhavet sampled in 2008 at a depth of 60 m.

Gälnan sub-area R

In Gälnan clear improvements have occurred in recent years. Even at the largest depth found so far, 31 m, the upper 5 cm is oxidized and probably bioturbated (**Fig. 1-22**). At 27 m the improvement occurred earlier and the upper 10 cm is more or less bioturbated. By using the same approach as described concerning Torsbyfjärden and combining it with a sediment accumulation rate of 0.8 cm yr^{-1} in the layers 15-25 cm (**Fig. 1-22**), the improvement started at 27 m in 2001-2002 and at 31 m in 2005.

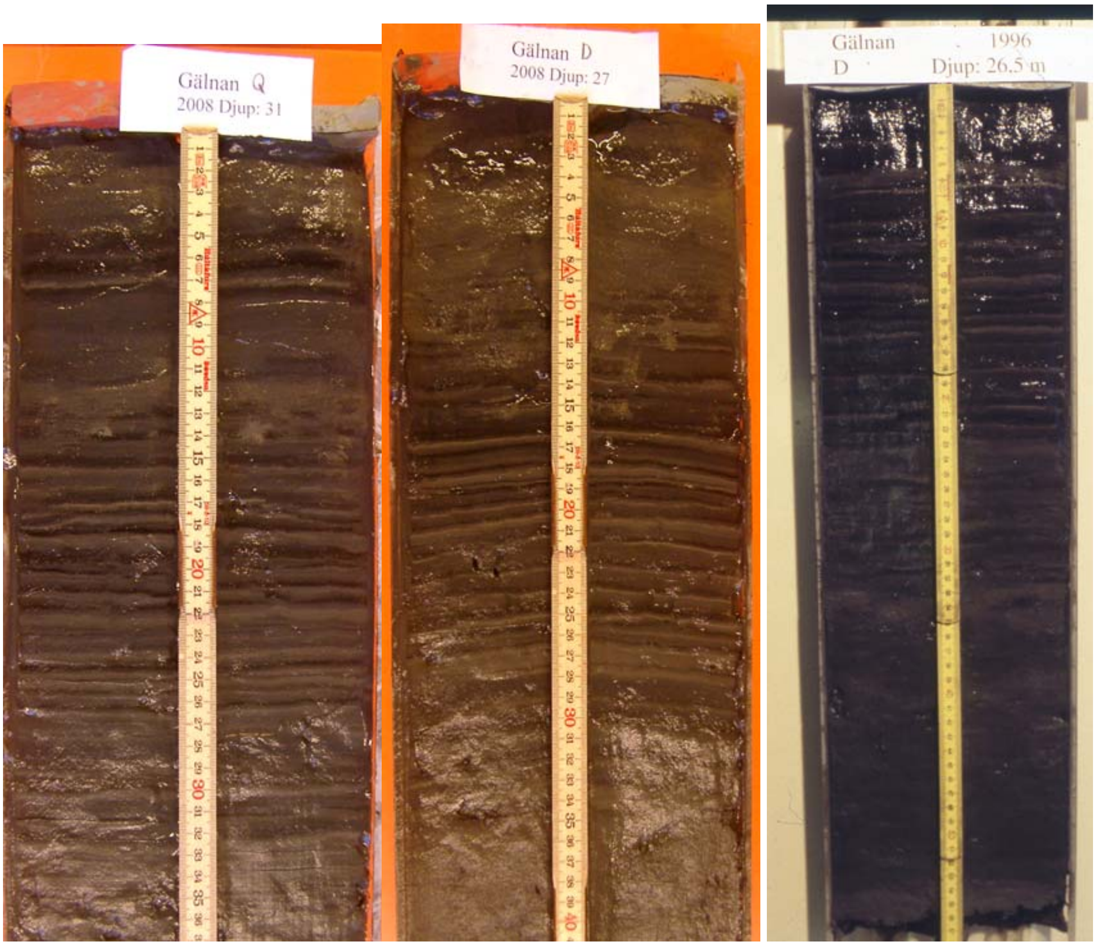


Figure 1-22 Photographs of sediment cores from Bay Gälnan from left to right 1/ 2008 depth 31 m, 2/2008 depth 27 m, 3/ 1996 depth 26,5 m.

Edöfjärden sub-area Q

From the results in Anon. (1997) one can conclude that the upper limit for lamination in Edöfjärden in 1997 was at approximately 20 m. The core from 21 m in the 1997 investigation is clearly laminated to the surface sediment (**Fig. 1-23**). The core from 31 m in 2008 shows a similar development, whereas the core from 27 m has an oxidized surface layer of 2 cm. This could indicate a recent improvement in the benthic environment. However, since the oxic layer is so thin it could also be a sign of a temporary improvement. Examination of more cores at shallower depths is needed to find out if the situation has improved.

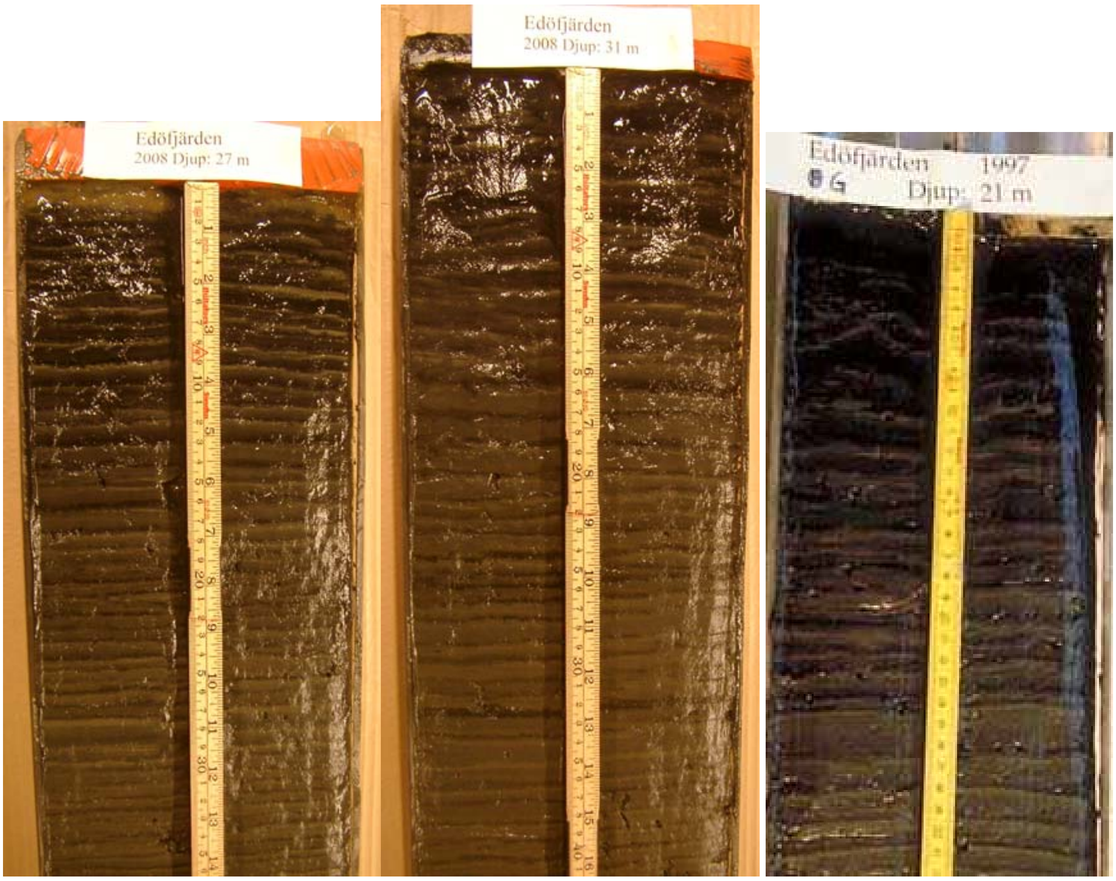


Figure 1-23 Photographs of sediment cores from Bay Edöfjärden from left to right 1/ 2008 depth 27 m, 2/2008 depth 31 m, 3/ 1997 depth 21 m.

Erstaviken sub-area M

Erstaviken is to be considered as a bay at the boundary, between the inner and middle archipelagos. In the deeper parts laminated sediments are still being deposited (**Fig. 1-24**). At 53 m 4 cm of oxidized and probably bioturbated sediments overlay a laminated sediment, thus indicating improving conditions during the last two years.

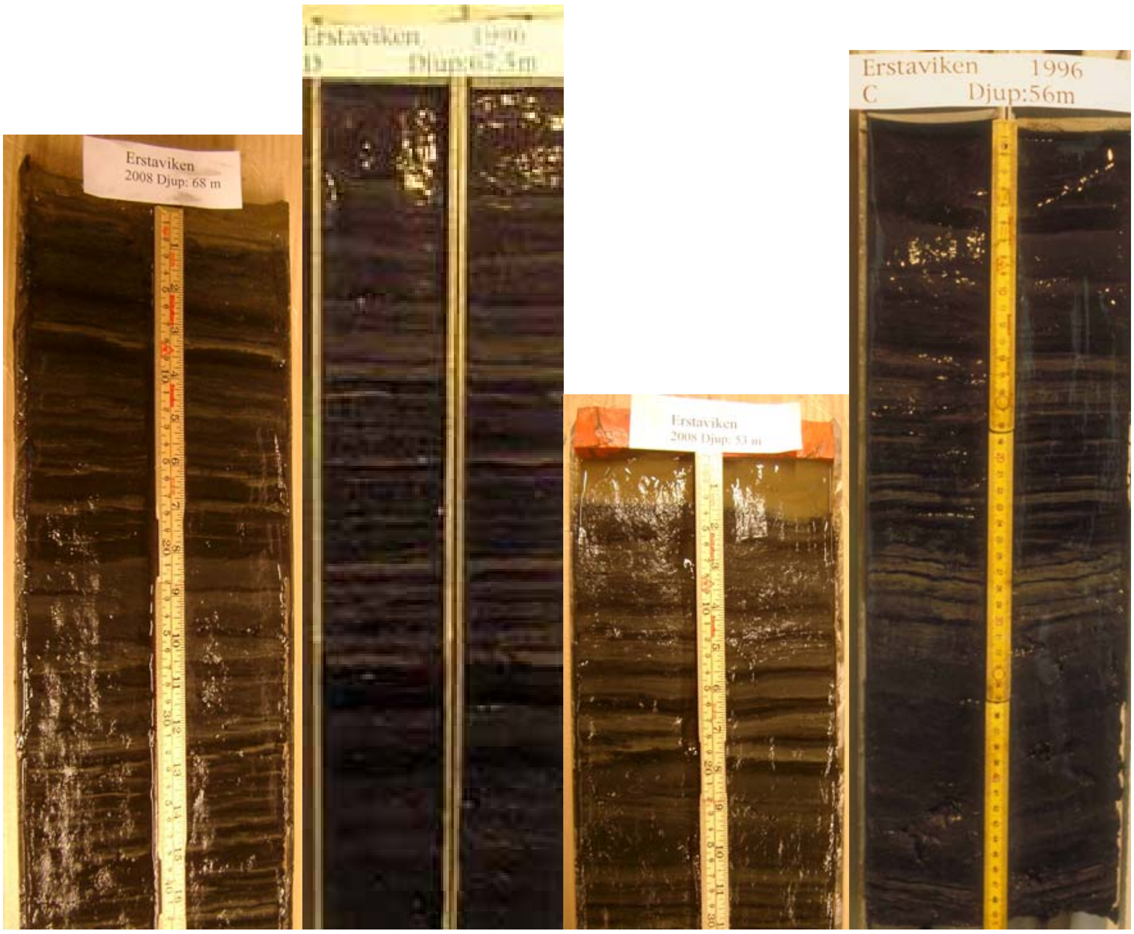


Figure 1-24 Photographs of sediment cores from Bay Erstaviken from left to right 1/ 2008 depth 68 m, 2/1996 depth 67,5 m, 3/ 2008 depth 53 m, 4/ 1996 depth 56 m.

Sandemarsfjärden sub-area O

Only one core was taken in 2008 in the Sandemarsfjärden Bay. Very clear lamination is shown in the core from 25 cm up to 2-3 cm from the surface (**Fig. 1-25**). Above this the sediment is oxidized and bioturbated. The number of laminas in the laminated layer is 31. In the core from 2001 the number of laminas is 27 and the core is laminated all the way up to the sediment surface. A comparison between the two cores indicates that the bioturbated layer in the core from 2008 consists of 3 years of sediment accumulation, which implies that the oxygen conditions improved substantially in 2006. The investigation in 2001 (Anon., 2001) indicated that the upper limit for lamination in the more exposed part of the bay was at 25 m To confirm this possible improvement cores need to be examined from 25 and 26 m.

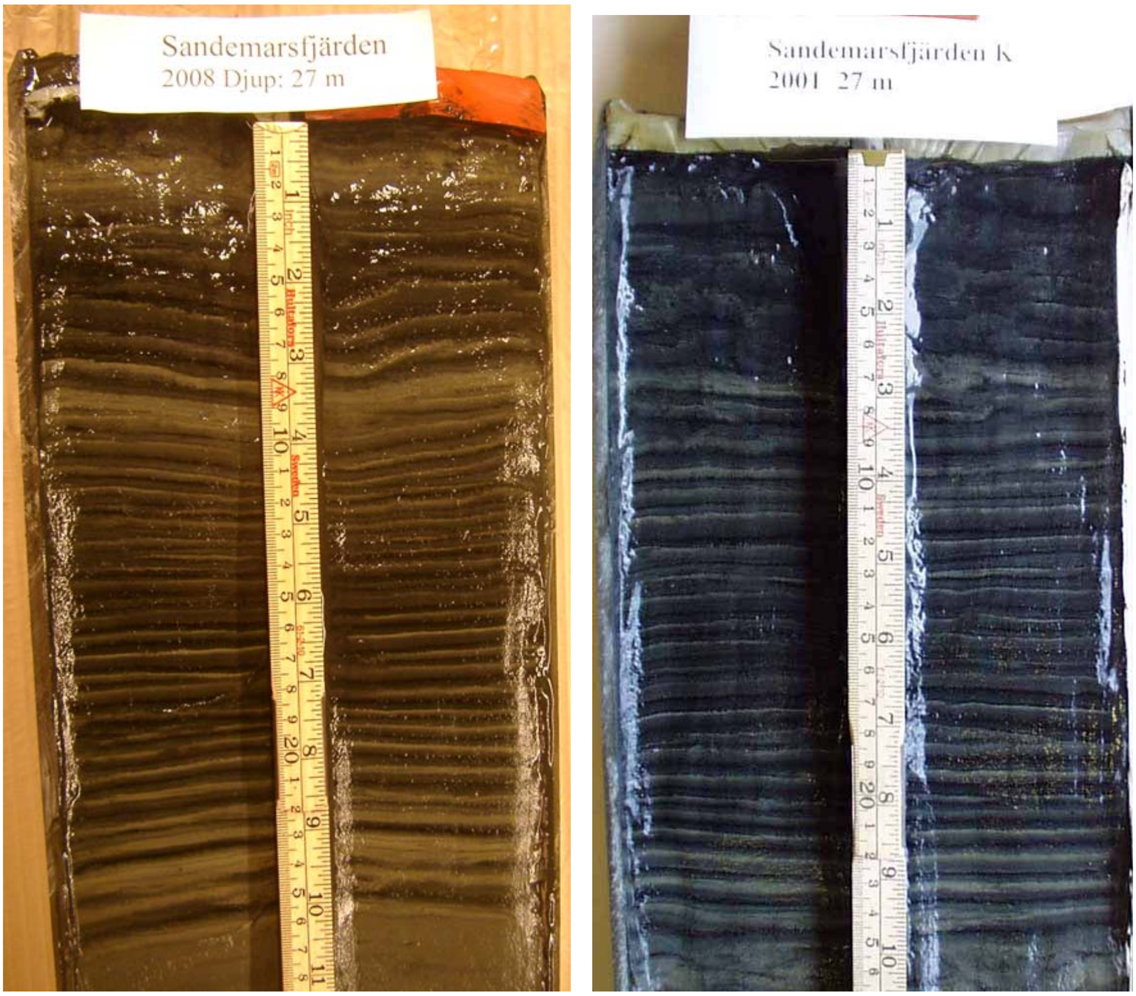


Figure 1-25 Photographs of sediment cores from Bay Sandemarsfjärden from left to right 1/ 2008 depth 27 m, 2/ 2001 depth 27 m.

Möja Söderfjärd sub-area S

In Möja Söderfjärd only one core was taken in 2008 at 105 m water depth. The core was laminated all the way up to the sediment surface showing that no improvements occurred in the deep water in recent years.

Outer archipelago

Pilkobbsfjärden sub-area U

In the year 2000 sediment investigation 9 cores were sampled at depths between 35 and 58 m. All cores were laminated in the surficial sediment. In 2008 lamination was observed in the upper parts of the cores that were sampled from 58 and 47 m (**Fig. 1-26**) whereas the core from 43 m shows a mixed and possibly bioturbated layer of 6-7 cm in the upper part. However, the stratigraphy of this core is somewhat peculiar indicating a hiatus at approximately 35 cm depth. This core may have been taken on a slope and therefore should be interpreted with due reservation. It is probable that improvements have occurred but more information is needed to judge.

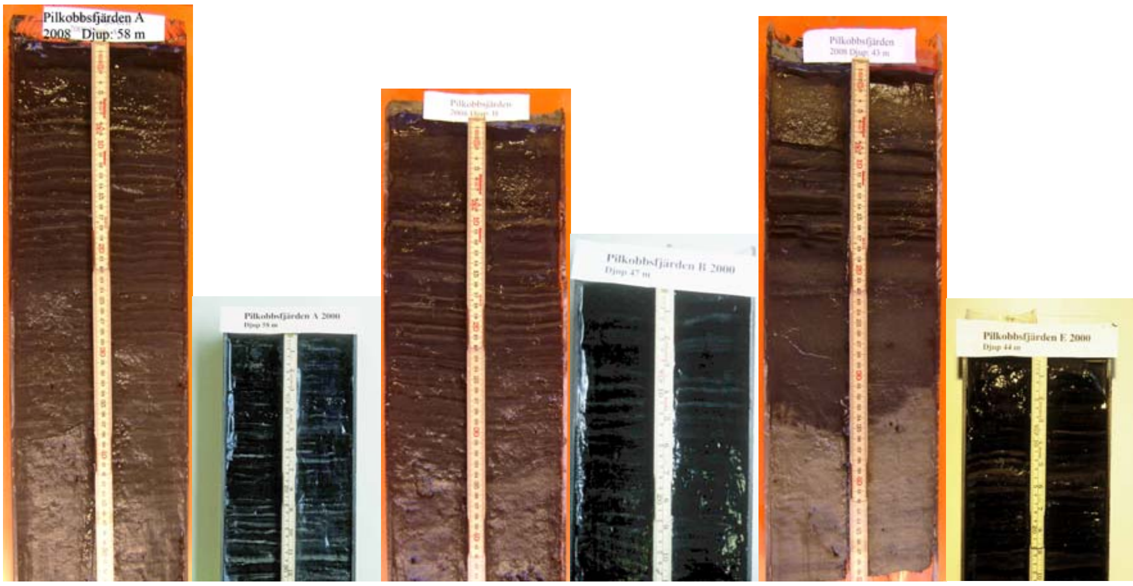


Figure 1-26 Photographs of sediment cores from Bay Pilkobbsfjärden from left to right 1/ 2008 depth 58 m, 2/ 2000 depth 58 m, 3/ 2008 depth 47 m, 4/ 2000 depth 47 m, 5/ 2008 depth 43 m, 6/2000 depth 44 m..

Bulleröfjärden sub-area T

In 1997 13 cores were taken between 34 and 51 m (Anon., 1997). In the southern part (**Fig. 1-27**), which is more exposed to the open sea, the sediment accumulation conditions varied widely with glacial clay at 51 m and a partly recently laminated sediment at 49,5 m. In the more sheltered northern part laminated sediments were deposited at depths exceeding 37 m. In 2008 laminated sediments were deposited at 47 m (**Fig. 1-28**). A sediment core from 41 m in Bulleröfjärden shows a similar and possibly disturbed stratigraphy as the core from 43 m in Pilkobbsfjärden. In the case of Bulleröfjärden more cores need to be taken to establish whether any improvements have occurred or not.

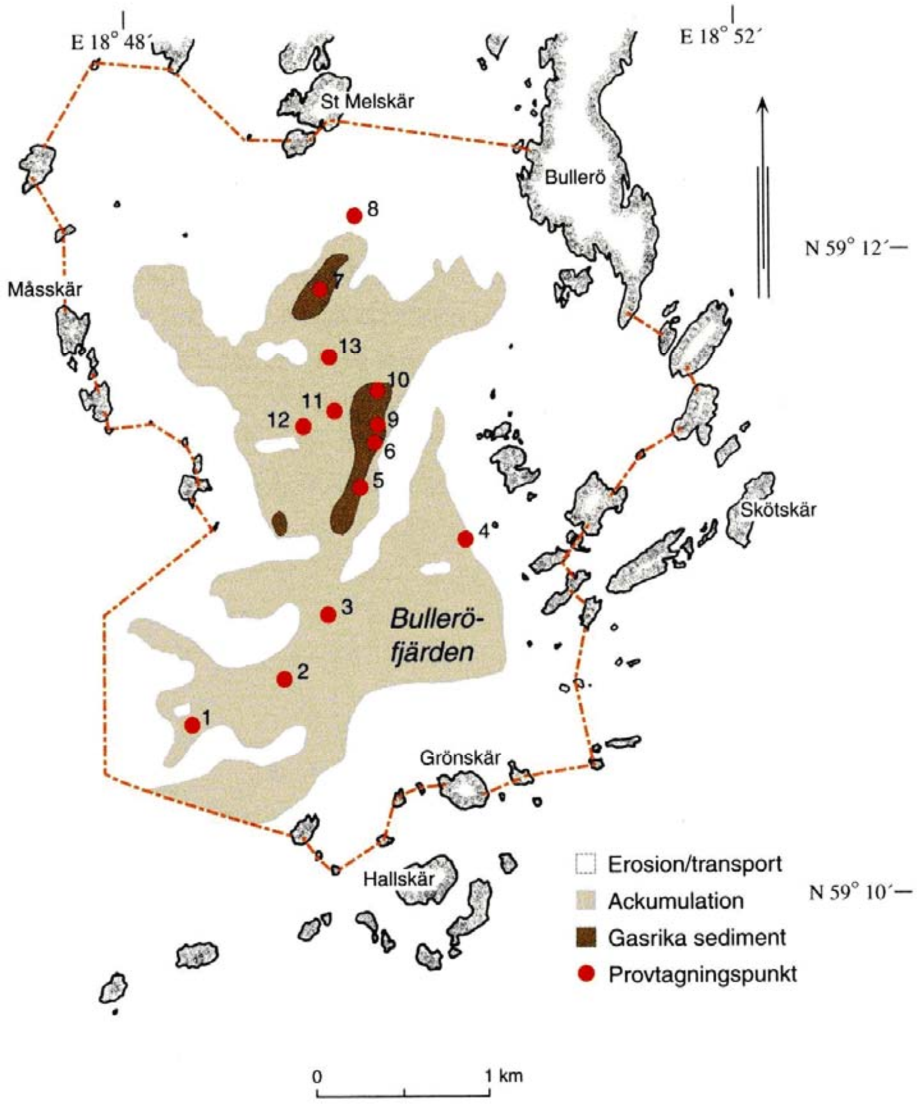


Figure 1-27 Bottom dynamic map of Bulleröfjärden. From Jonsson et al. (2003).

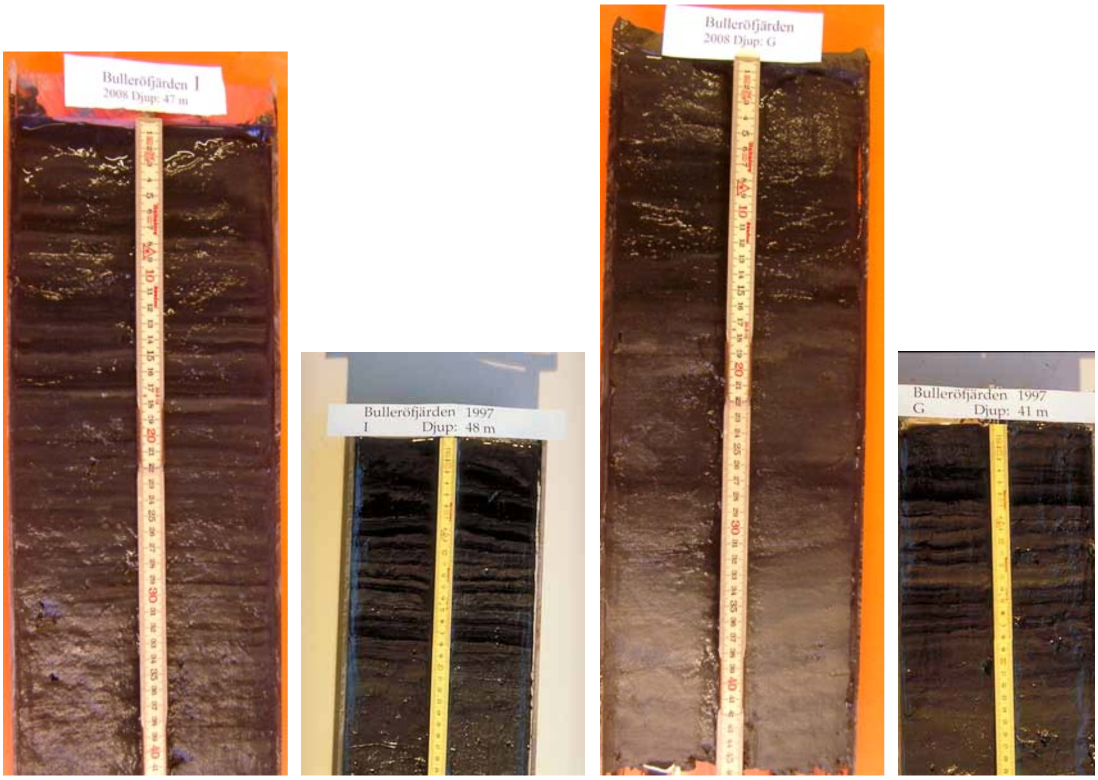


Figure 1-28 Photographs of sediment cores from Bay Bulleröfjärden from left to right 1/ 2008 depth 48 m, 2/ 1997 depth 48 m, 3/ 2008 depth 41 m, 4/ 1997 depth 41 m..

1.3.2 Comparisons with benthic fauna investigations

In **Table 1-2** the results from present examinations of sediments and macrofauna are compared with equivalent sampling excursions in the late 1990s. During the 1990s the surface sediments were black indicating anoxia at all 9 visited deep areas in the inner archipelago. In 2008 only 3 of 12 surface sediments were reduced. This apparent improvement of oxygen conditions in the sediments is statistically significant at the 0.99 level applying the statistical methods described in the methodology chapter. An almost identical pattern was found when comparing the results from benthic fauna studies in 1998 and 2008 respectively. In 1998 benthic fauna were absent or at least considerably impoverished (biomass< 0.5 g/m^2) at 10 of 12 visited areas. In 2008 macrozoobenthos was absent from only 2 of 11 stations. A statistically significant change was determined at the 0.99 level. Furthermore these results suggest an absolute correlation between the interpretations of sediment versus macrozoobenthos data.

Table 1-2 Comparison of results from recent investigations of sediments and macrozoobenthos with equivalent investigations in late 1990's data from this study, Anders Stehn, Eurofins Environment, pers. comm., Lännergren et al., 2007 and Jonsson et al., 2003

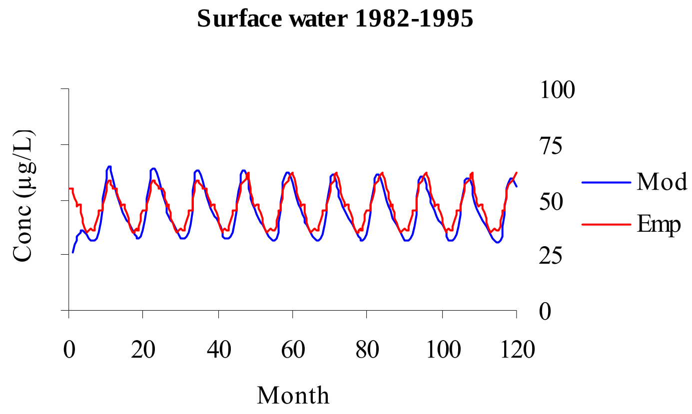
Sub-area	*Depth*	*Surface sediment*		*Macrofauna*	
	(m)	*1996-1999*	*2008*	*1998*	*2008*
A (Waldemarsudde)	*30*	*Black*	*Oxidized*	*0**	+
B (Lilla Värtan)	*30*	*Black*	*Oxidized*	*0*	+
C (Stora Värtan)	*20*	-	*Black*	*0*	-
D (Askrikefjärden)	*30*	*Black*	*Oxidized*	*0*	+
E (Höggarnsfjärden)	*40*	*Black*	*Oxidized*	*0***	+
F (Långholmsfjärden)	*30*	*Black*	*Oxidized*	*0*	+
G (Torsbyfjärden)	*50*	*Black*	*Oxidized*	*0*	+
H (Solöfjärden)	*50*	*Black*	*Oxidized*	*0*	+
I (Trälhavet)	*60*	*Oxidized****	*Oxidized*	+	+
J (Farstaviken)	*10*	*Black*	*Black*	*0*****	*0*
K (Baggensfjärden	*50*	*Black*	*Black*	*0*	*0*
L (Ägnöfjärden)	*40*	-	*Oxidized*	+	+

+ Present, 0 Absent (biomass < 0.5 g/m^2), - No data * 20 m water depth **30 m water depth ***Data from year 2000

1.3.3 Mass balance calculations

In **Figure 1-29** the phosphorus concentration in surface water and in deep water is shown during ten years of simulation representing mean values for 1982-1995. The driving variables are identical during the ten years. We will point out two observations: 1) The overall fit of the model is good, indicating that the description of fluxes is correct. The best fit is obtained after half the simulation time. 2) The system is not in a steady state; the phosphorus concentration is decreasing. Hence we expect lower phosphorus concentrations in the future if the phosphorus inflow is constant. In **Figure 1-30** the same model parameters are used for the period 1996-2007. We observe that the model fit is also good for this period. The modelled phosphorus fluxes to and from the sediments for the two periods are presented in **Table 1-3**.

a)



b)

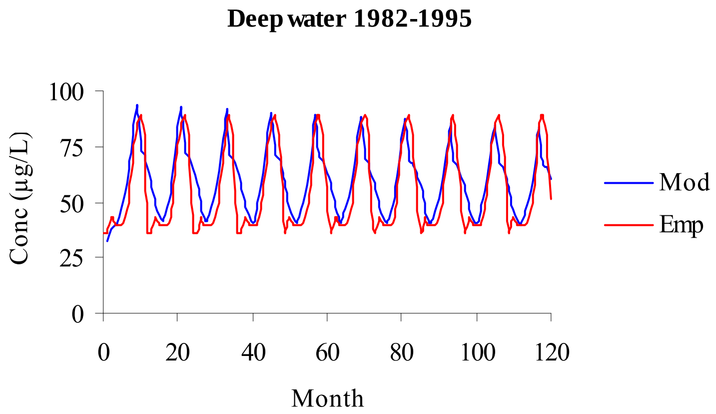
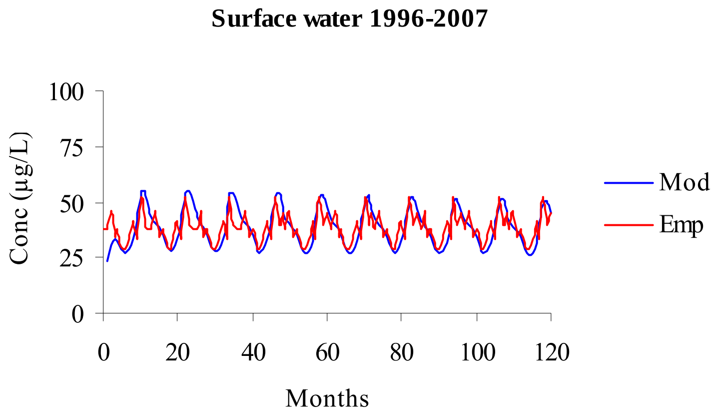


Figure 1-29 Modelled and empirical phosphorus concentration 1982-1995 in a) surface water and b) deep water. The empirical values are monthly mean values. The monthly driving variables are constant during the simulation period but the total phosphorus pool is apparently decreasing.

a)



b)

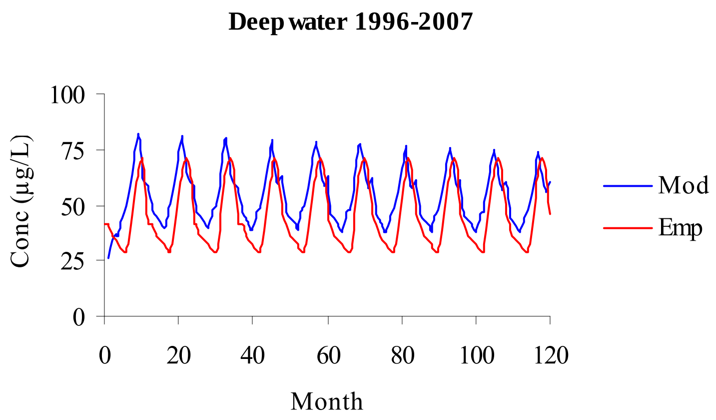


Figure 1-30 Modelled and empirical phosphorus concentration 1996-2007 in a) surface water and b) deep water.

Table 1-3 Modelled annual phosphorus fluxes (tonnes) to and from the sediments for the periods 1982-1995 and 1996-2007.

Annual (tonnes)	1982-1995	1996-2007
Sedimentation	393	333
Resuspension	309	261
Diffusion	261	226

The calculated phosphorus release from the area is around 3 $g \cdot m^{-2} \cdot yr^{-1}$ for the period if assuming that diffusion occurs on 2/3 of the total benthic area. However, calculations presented in Part B of this report based on analysis of sediments cores from Torsbyfjärden contradict this result. Keeping in mind that the two sediment cores that were examined only represents a small fraction of the total bed area of the inner archipelago, they indicated not a sediment release but a net accumulation of phosphorus in this sub-area. **Figure 1-31** summarizes the fluxes of phosphorus to the inner archipelago for the two studied periods. The estimated P release from the sediments is of the same order of magnitude as the inflow from Trälhavet but larger than the sum of discharges from Lake

Mälaren and Stockholm's sewage treatment plants (STPs). When comparing the period 1982-1995 with 1996-2007 the inflow of P has decreased around 15 % or approximately 120 tonnes/yr. The transport through river Norrström has decreased from 180 to 150 tonnes/yr, in STPs from 60 to 30 tonnes/yr, within the sediments from 260 to 225 tonnes/yr and from the outer archipelago from 270 to 250 tonnes/yr.

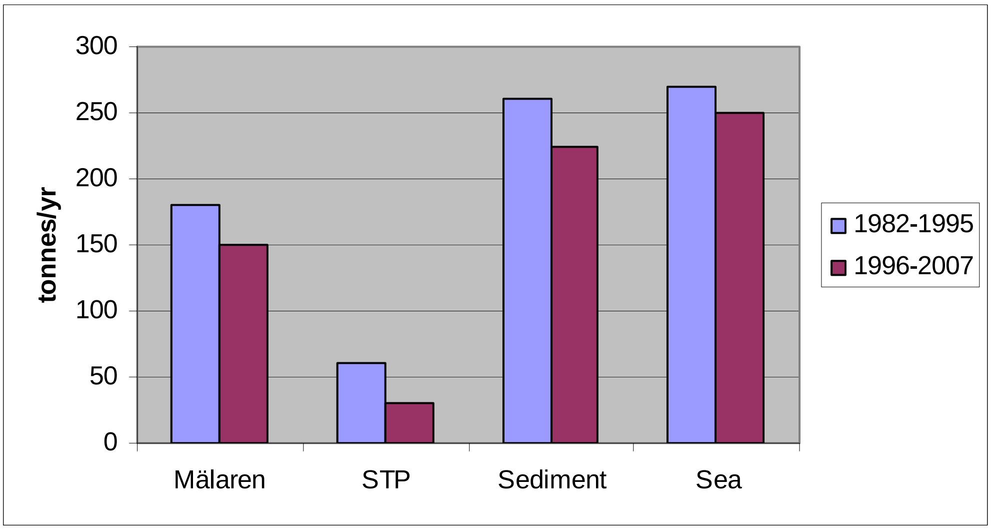


Figure 1-31 A summary of calculated fluxes of phosphorus **to** the inner archipelago for the periods 1982-1995 and 1996-2007 respectively. The fluxes are discharges from Lake Mälaren and from City of Stockholm sewage treatment plants (STP), net release from sediments and inflow through water exchange with outer archipelago (Sea).

In **Figure 1-32** a mass balance calculation for total nitrogen turnover in the inner archipelago is presented. Compared to the above shown calculations for phosphorus the modelling approach was simplified (the water column was not divided into surface and deep water volumes and the seabed was not divided into sedimentation and non-sedimentation areas). The main reason for this is that to our best knowledge, no validated mass balance models exist for nitrogen in Baltic coastal areas. Compared to phosphorus, the reduction in inputs of total nitrogen has been larger, around 35 % or approximately 5 000 tonnes/year. The estimated N release from the sediments due to mineralization of organic bound nitrogen was relatively less important than for phosphorus. The transport through river Norrström has decreased from 4 200 to 3 500 tonnes/yr, in STPs from 4 100 to 1 800 tonnes/yr, within the sediments from 2 500 to 1 300 tonnes/yr and from the outer archipelago from 3 900 to 3 100 tonnes/yr.

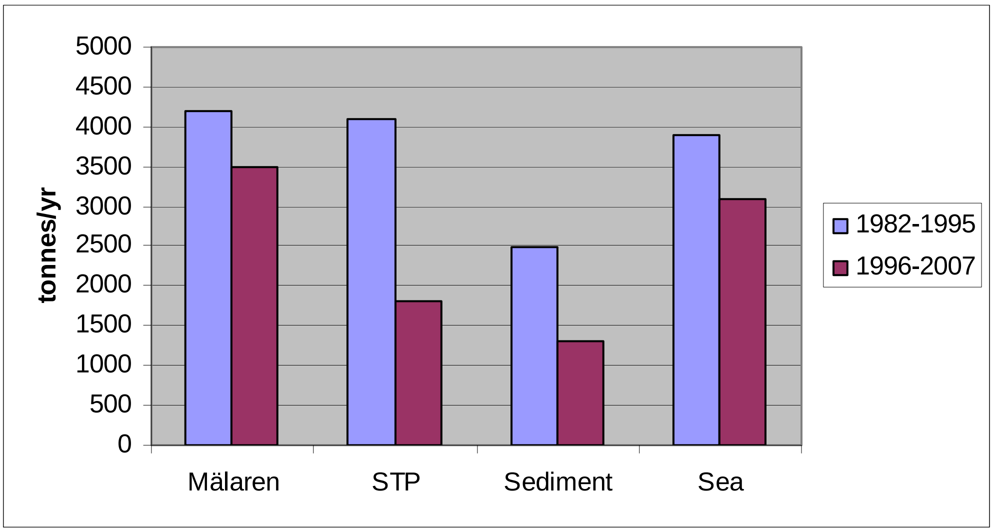


Figure 1-32 A summary of calculated fluxes of total nitrogen to the inner archipelago for the periods 1982-1995 and 1996-2007 respectively. The fluxes are discharges from Lake Mälaren and from City of Stockholm sewage treatment plants (STP), diffusion from sediments and inflow through water exchange with outer archipelago (Sea).

In **Figure 1-33** a mass balance calculation for ammonia (NH_4-N) turnover in the inner archipelago is presented. Compared to the above shown calculations for phosphorus and total nitrogen the sediments do not act as a net source. It is likely that there are mineralization processes within the sediments transforming organically bound nitrogen into ammonia but to satisfy the mass balance equation it was necessary to include a rate simulating the nitrification bacterial process transferring ammonia into nitrate. For the period 1982-1995 the annual nitrification was calculated to average 600 tonnes. For the period 1996-2007 nitrification averaged 400 tonnes/yr. The reduced nitrification is to a large extent explained by massive reduction in NH_4-N discharge from STP (from 2 200 to 500 tonnes/yr). In total, the ammonia input to the inner archipelago has decreased by around 75 % or 1 700 tonnes/yr between the studied periods.

The nitrification of ammonia to nitrate is an oxygen consuming process taking place when water temperature exceeds +10°C. Chemically nitrification is a two step reaction, which stochimetrically can be written as

$$2NH_4^+ + 4O_2 \rightarrow 2NO_3^- + 2H_2O + 4H^+$$

From a mass perspective this means that 1 g of ammonia consumes 3.6 g of oxygen. Theoretically a reduction in nitrification of 200 tonnes/yr therefore would lead to an increased oxygen level in the bottom water of around 0.1 mg/l assuming an equal distribution in the water volume of the Inner archipelago.

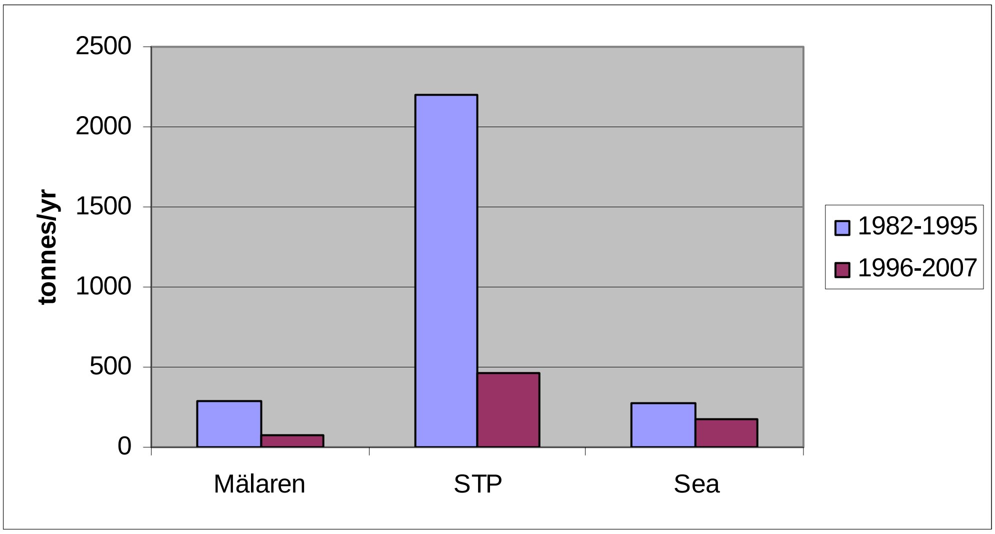


Figure 1-33 A summary of calculated fluxes of ammonia (NH_4-N) **to** the inner archipelago for the periods 1982-1995 and 1996-2007 respectively. The fluxes are discharges from Lake Mälaren and City of Stockholm sewage treatment plants (STP) and inflow through water exchange with outer archipelago (Sea.)

1.4 Discussion

By comparing the stratigraphy of recent sediment cores with cores taken in the 1990s we have shown that clear improvements occurred in two bays in the inner Stockholm archipelago from around 2004 and onwards. Increased oxygen concentrations in the near-bottom water have restored the living conditions for organisms in the sediment/water interface over large areas. This has been shown in the comparative study of sediment stratigraphy and benthic macro fauna abundance. The results show that anoxia still prevails only at depths larger than 45-50 m. There is one exception in the enclosed bay Farstaviken. From the sediment comparisons of the sediments of Torsbyfjärden, Solöfjärden and Baggensfjärden one can conclude that anoxic/hypoxic conditions regularly occurred in large bays in the inner archipelago as shallow as at water depths of 15-18 m.

Clear improvements have also been detected in three of the seven bays investigated in the middle archipelago. In some of the other bays there are oxidised surface sediments at formerly anoxic/hypoxic sites that may be indicative of trends of improving oxygen conditions in the deep water. However, until more cores have been examined these indications should be considered with due reservation. In the outer archipelago no clear signs of improving conditions have been observed, although the number of cores is too few to clearly judge the situation.

It is interesting to put the results from this study into perspective by analyzing the potential increase in secondary biological production in the inner archipelago that might arise when the deep water oxygen situation obviously have improved. Most of the research on this topic has been focused on shallow bottoms (see e.g. Rosenberg, 1985; Thrush et al., 2006; Stål, 2007). For example, Stål et al. (2008) found that a one km^2 increase in the availability of shallow soft sediment bottoms along the Swedish west coast would give an increase in profits in the plaice fisheries amounting to a value of about SEK 300-360 millions over a 55 year time period. However, in the Baltic Sea the production potential decreases dramatically with increasing water depths. Rosenberg (1985) found that the biomass of infauna in the Baltic Sea on average was 100 g/m^2 on depths between 5 and 25 m while decreasing to 30 g/m² at larger water depths. Simultaneously, the production capacity of infauna expressed as yearly production/average biomass was roughly 5 times lower in deep waters (46 m) compared to shallow coastal habitats (Rosenberg, 1985).

The recolonization of bottoms by macrozoobenthos found in this study is to a high degree associated with soft bottoms below 25 meters water depth. According to the previous paragraph the value of this improvement in terms of ecosystem function is rather low. It should however be emphasized that the signal of improving conditions for macrofauna in deep areas is also likely to be reflected in improving conditions at shallower depths more important for e.g. fish production.

Recovery from hypoxia has been reported from a number of pulp mill recipients in Scandinavian waters (Lindeström, 1995; Afzelius, 1996; Karlsson et al., 2005 (**Fig. 1-34)**; Bernes, 2006; Grahn et al., 2006). The reason for oxygen deficiency in pulp mill recipients has primarily been a high loading of allochthonous carbon from wood fibres in the effluents. After upgrading of the technical standard within the mills and installing of effluent treatments from the late 1960s onwards the oxygen situation has gradually improved in many primary recipients as the old fibre banks have been degraded. Historically the inner Stockholm archipelago has also been the primary recipient for a large amount of organic matter and nutrients before improved waste water treatment was established in the 1970s. Brattberg (1986) found that the water quality in the inner archipelago improved significantly shortly after reducing the input of nutrients from municipal sewage water. Jonsson et al. (2003) concluded however, that the signs of improved water quality not was reflected in the benthic environment since the area of bottoms predominated by laminated sediments did not decrease during the 1990s. At this stage, it can not be ruled out that the signs of improving oxygen conditions we have seen in this study are a lag phenomena explained by the degradation of older deposits rather than a decrease in recent settling of organic matter.

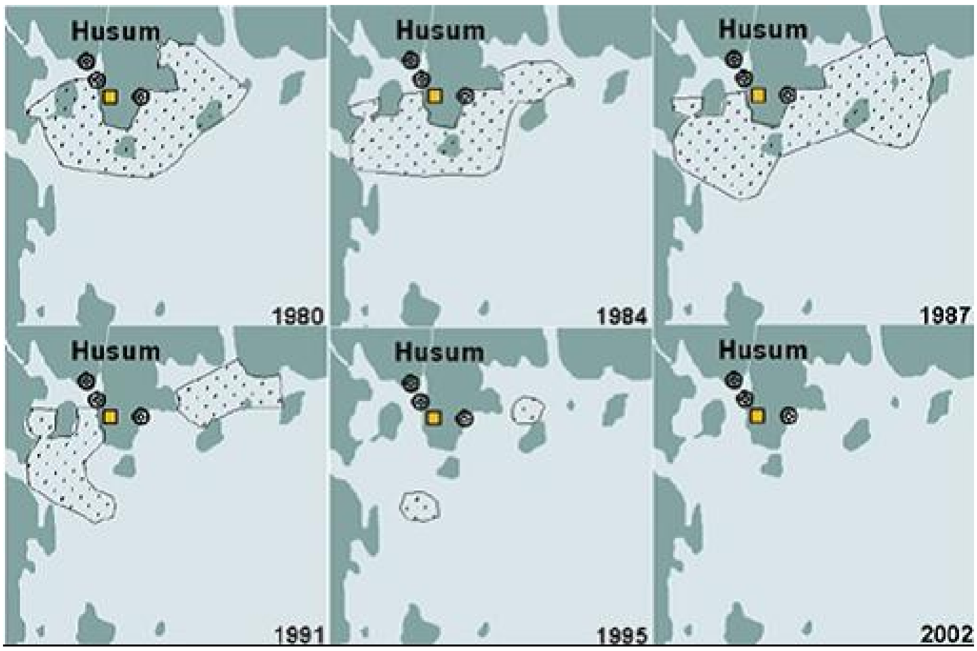


Figure 1-34 Successive reduction of areas with anoxic surface sediments (dotted areas) outside Husum Mill, Sweden's largest pulp producer, situated along the coast of Bothnian Sea. From Karlsson et al. (2005).

The historical load to inner archipelago from City of Stockholm and Lake Mälaren between 1940 and 1970 was approximately 1 200 tonnes P/yr (Bernes, 2005; www.ma.slu.se). We have also run the mass balance for phosphorus under these premises and found that under these conditions the sediments functioned as a net sink for phosphorus (approximately 100 tonnes/yr). It is therefore reasonable that a store of phosphorus was built up during this period which is now successively being emptied leading to the predicted net release during recent years. Having a model that seems able to successfully reconstruct the fate of phosphorus during a period of massive input followed by a transition state where the old deposits are being mineralized, it would of course be very tempting to predict for how long the sediments will act as net source before steady state is reached. However we have refrained from this, mainly because there are very few empirical data behind the estimate of the total store of mobile phosphorus in the inner archipelago. It would be very interesting in the future to expand the investigations of sediment bound phosphorus to cover all the common bottom types in the inner archipelago. The area's relative enclosedness in combination with good availability of empirical data from the water column through the Environmental Monitoring Programme makes it suitable for comparative studies using models together with empirical data collection (see further discussion in part B).

Lännergren et al. (2007) suggested that the installation of nitrogen removal within City of Stockholm STP in combination with reduced emissions of organic carbon could be one of the factors behind the observed improved oxygen conditions in the water column of the inner archipelago. Our mass balance calculations showed that the reduced emissions of ammonia have lowered oxygen consumption by approximately 0.1 mg/l. The total reduction in BOD emissions from STPs for the studied period have been around 10 000 tonnes/yr (Lännergren et al., 2007). It is interesting to put these numbers into perspective by comparing them with the autochthonous input of carbon through primary production. There is a general formula relating primary production in g C/m^2, day to chlorophyll-a concentrations in surface water, Secchi depth and water temperature (Håkanson et al, 2004**)**. Using available data from Stockholm Water database led to a calculated average carbon fixation in the whole area of the order 75 000 tonnes C/year or 1.9 g C/m^2, day. In comparison, the TOC transport through Norrström averaged around 40 000 tonnes year during the period 1996-2007. Even if assuming a rather low BOD number (Wilander, 1988) for the primary produced matter, the theoretical oxygen demand in the water column to mineralize this amount would be of the order of 0.5 mg/l. To summarize, it is not likely that the improved waste water treatment by installing nitrification zones in the City of Stockholm STP in the mid 1990s was an important factor behind the observed improvement in oxygen conditions since the fluxes of oxygen consuming matter discharged from the STPs are overwhelmed by autochthonous carbon.

However, carbon fixation through primary production also requires nutrients and therefore our next step should be to examine the importance of nutrient levels. For example Rydberg et al. (1990) took an experimental approach in an effort to follow the coupling between increasing nutrient supplies and decreasing deep-water oxygen concentrations in Kattegat, the estuary of the Baltic Sea. They found that the oxygen consumption in the deep water was well correlated with the external supply of nitrate to the surface water, which in turn is an indirect measure of the settling of oxygen consuming seston. Håkanson & Bryhn (2008) have found small but statistically significant decreasing trends in concentrations of Chlorophyll-a and total phosphorus in the surface water of open Baltic Proper when evaluating the period 1974-2006. In agreement, both nitrogen and phosphorus levels have also decreased in the inner archipelago resulting in lower Chl-a levels (**Tab. 1-1**) when comparing the period 1982-1995 with 1996-2007. Moreover Secchi depth has also increased from 3.4 to 4.2 m (**Tab. 1-1**). Therefore it is not straightforward to conclude that primary production has decreased proportionally to the decrease in Chl-a concentrations since an increased Secchi depth implies a larger depth of the photic zone. Although algae production in the surface layer has decreased this might is compensated by a stimulated production of macrophytes, benthic algae and micro algae further down in the water column due to an enhanced light climate.

Håkanson (1999) developed an effect-load-sensitivity model for the mean summer oxygen saturation in the deep water zone of Baltic coastal areas. The model was derived using data from 23 coastal areas. A correlation was found between oxygen saturation, load factors related to nitrogen and phosphorus concentrations in water and sensitivity factors related to the size and form of the coast. The degree of explanation was almost 90 % (r^2=0.89). However, putting our nutrient levels into Håkanson's (1999) model was not fruitful since they were outside the model domain i.e. the nutrient levels were higher than in any of the areas the model was developed for.

It is likely that the observed decreases in nutrient levels in the water column are partially a consequence of a decreased leakage from the sediments (**Fig. 1-31**, **1-32**) indicating that the inner archipelago might have turned into a self amplifying transition state, where the amount and thereby the breakdown of old nutrient loaded deposits has decreased → less oxygen consumption and less mineralisation of nutrients → less primary production in the water column → less settling of seston → less oxygen consumption in the bottom water → faster decomposition of remaining deposits.

An alternative explanation, which is discussed in more detail in Part B of this report, assumes that the mobile phosphorus pool present in sediment layers is not older than a decade. One explanation for this pattern could be a continuous recycling of bioavailable P that entered the system several decades ago, e.g. after completion of municipal sewage treatment plants. With limitations in burial processes, the only possible other main loss process would be export to the outer archipelago, resulting in the lag phase in recovery.

Persson and Jonsson (2000) suggested that the improving conditions that were registered in the outer St. Anna archipelago in the early 1990s were due to the increasingly windy conditions causing water turbulence to greater depths than during calm conditions. To judge whether the reason for improving oxygen concentrations in the deep water could be related to more windy conditions in the early and mid 2000s, Persson and Jonsson (2000) chose the long time series of wind speed registrations at Gotska Sandön to be indicative of the wind situation in the northern Baltic Proper. In **Figure 1-35** we have compiled wind data for the years 1951-2006. Interestingly, all of the years 2000-2006 were less windy than any other year registered since 1951. Provided that the wind registrations at Gotska Sandön are representative for the overall wind situation in the Stockholm archipelago, we can thus falsify that more windy conditions in the 2000s could be the reason for the registered improvements in the Stockholm archipelago.

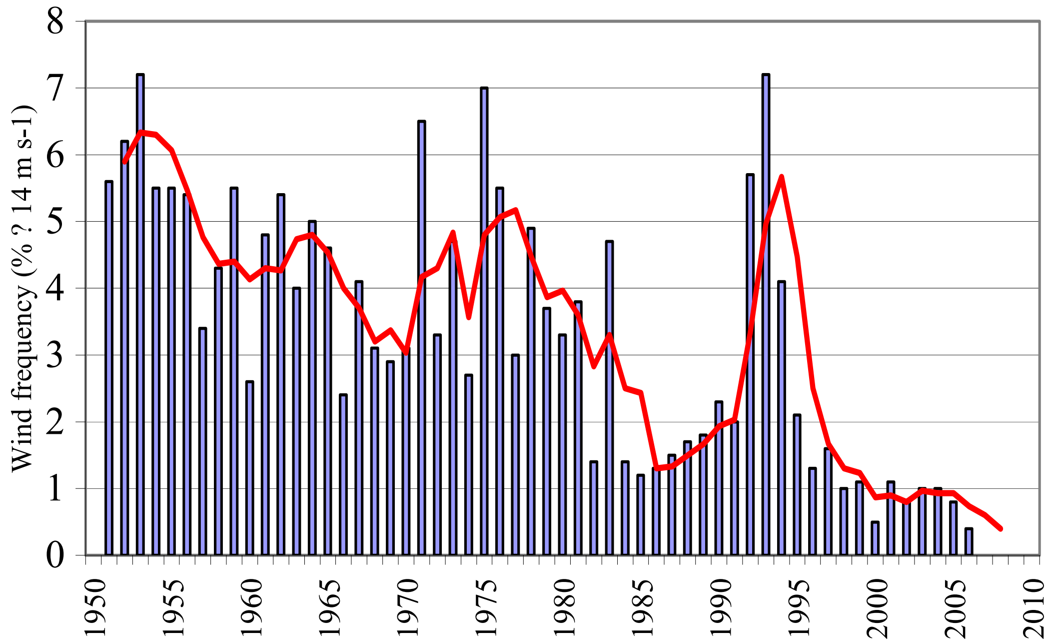


Figure 1-35 Frequency of wind speed ≥ 14 m s^{-1} at Gotska Sandön. Red line indicates running three year average. Unpublished data from SMHI.

Having gone through the alternative explanatory models for the observed improvements in oxygen conditions along the sediments of inner Stockholm archipelago our conclusion is that the observed changes to a large extent is due to the decomposition of historically deposited organic matter similar to what has have been observed in several other Scandinavian recipients with high historical load. More than 20 years after Brattberg (1986) published her pioneering work about improved water quality in the inner archipelago after tertiary sewage treatment was established in the 1970s reducing the land based input of nutrients by a factor of five or more the sediments have now also responded to the treatment. Nevertheless, we have also seen a clear indication of improvements in the middle archipelago, which to a much less degree have been affected by discharges from City of Stockholm and the catchment of Lake Mälaren. It is therefore of great importance to expand the investigations from this study to other well documented archipelago areas which historically also have been suffering from hypoxia but not to the same extent have been affected by discharges from a large city e.g. parts of the coastline along the counties of Östergötland, Södermanland and Uppland. A positive development with decreasing areas of hypoxia in these areas too would imply a large scale improvement of Baltic Sea environmental conditions.

1.5 Conclusions

- A considerable and statistically significant improvement of the benthic conditions was found in the inner archipelago when comparing results from sediment and macrozoobenthos surveys from the 1990s with the present situation.

- In the middle archipelago a remarkable recovery of oxygen conditions was also found on deep soft sediment bottoms. However, in the outer archipelago we did not find any changes. However, the data set from this area is limited.

- There was good correlation between the interpretation of sediment data and the measured macrozoobenthos biomasses.

- The main explanation to the improved conditions in the inner archipelago seems to be the breakdown and removal of old deposits originating from effluent discharges before tertiary waste water treatment was installed in the 1970s.

2 Part B-Phosphorus dynamics in sediments

2.1 Introduction

In this study, we address the role of the sediments for the Baltic Sea trophic status. Reduced conditions in the sediments promote phosphorus release to the water column, although originally everything contained in the sediments emanate from the overlying water mass. It is however well-known from lakes and coastal areas that the ability of sediments to bind phosphorus is reduced when the oxygen concentration decreases. This is a typical feedback mechanism in eutrophicated systems as oxygen is often rapidly consumed in bottom waters as a result of decomposition of large amounts of organic material (Mortimer, 1941; Nürnberg, 1984; Conley et al., 2002; Bernes, 2006).

The long term capacity of sediments to retain bio-available phosphorus is crucial for the phosphorus balance of the whole system. Also in oxic sediments, the oxygen concentration decreases downward in the sediment profile, and hence the redox potential decreases as sediment is transported downward in the profile when new material is deposited at the sediment surface. A few centimetres below the sediment surface there are always anoxic conditions and redox sensitive phosphorus fractions may be mobilized and diffuse upwards. Redox sensitive phosphorus fractions are mostly associated with iron compounds, although e.g. redox sensitive manganese species may also bind phosphorus (Mortimer, 1941; 1942). When reaching oxic surface sediments the mobilized phosphorus may be trapped again unless the surface is saturated with phosphorus (e.g. Matthiesen et al., 1998).

Baltic Sea sediments often experience shifts in oxygen conditions. When previously oxic sediments turn anoxic a pulse of phosphorus leakage from the surface sediments is experienced (Balzer, 1984; Koop et al., 1990). Such processes have probably contributed to varying phosphorus levels in the deep waters of the Baltic during the last decades. Whether these processes are reversible depends largely on the presence of iron available for trapping phosphate in surface sediments or deep water (Gunnars and Blomqvist, 1997). Besides this temporary binding of phosphate to iron, the quantitative importance of binding mechanisms that transforms phosphate in the sediment into inert complexes that gets permanently buried is largely unknown.

Another factor of potential importance is the rate of decomposition of phosphorus containing organic material. Slower decomposition is generally expected in anoxic environments and hence a larger proportion of organically bound phosphorus may be buried in anoxic sediments than in oxic sediments (e.g. Gächter et al., 1988). Oxygenation of reduced sediment could thus possibly increase the decomposition rate but fail to bind dissolved phosphate if iron is lacking in the surface sediment, due to iron sulphide formation (Blomqvist et al., 2004). The short-term effect of oxygenation is therefore uncertain.

Direct measurement of different fractions of phosphorus in depth profiles of sediments in different oxygen regimes obviously have the potential to provide crucial information about historical and present conditions and a basis to predict the development of the phosphorus dynamics in the system. Quantification of the amount of phosphorus that will eventually leak from the sediments to the water mass, the mobile phosphorus pool, is central for the quantification of phosphorus dynamics in the coastal zone. Identifying the speciation of this mobile phosphorus is central to predict when leakage will occur and how different restoration measures, such as oxygenation of bottom water, may increase the binding of phosphate to iron. Mobile phosphorus in Swedish lake sediments have been quantified in e.g. Lake Erken (Rydin, 2000; Malmaeus & Rydin, 2006) and in Lake Mälaren (Weyhenmeyer & Rydin, 2003). A number of lakes in the vicinity of Stockholm have also been investigated to prepare for lake restoration (Rydin, 2008 and references therein).

In this report we present data on phosphorus concentration and speciation in seven depth profiles and a number of surface sediment samples in different parts of the Stockholm archipelago with different historical and present oxygen conditions. Using these data we provide mass balances for phosphorus (sedimentation, burial, leakage) at the different sites by analyzing concentration changes of different phosphorus fractions in the sediment depth profiles. Comparing different bottom types facilitates interpretations and extrapolation to other parts of the Baltic Sea.

2.2 Methods

Sediment sampling
In total ten cores of sediments were collected with a Gemini double corer (inner diameter 80 mm) from four coastal areas (fig. 2-1) in November 2008. Core samples were sliced shortly after sampling in 2 cm layers down to 20 cm and at selected levels down to 60 cm. Surface samples from erosion and transportation areas (0-2 cm) were also taken. Deposition rates in individual cores were estimated through lamina counting and were found to be generally consistent with estimates given by Jonsson et al. (2003).

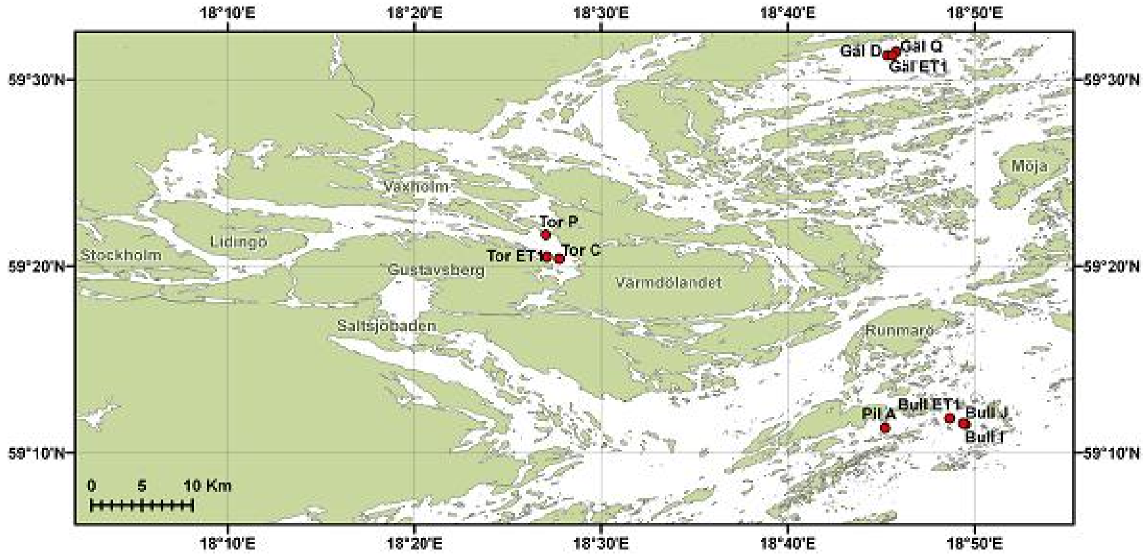


Figure 2-1 Locations of coastal areas where sediments were collected.

Chemical analyses
Chemical analyses were performed at the Erken laboratory (Uppsala University). All sampled cores were stored in darkness at 4° C until preparation in the laboratory.

The total amount of iron (Fe) and manganese (Mn) was measured on selected samples after melting with lithiummetaborate followed by dissolution in hydrochloric acid, by ALS Scandinavia AB.

Total phosphorus (TP) content in sediments was analysed as phosphate after acid hydrolysis at high temperature (340° C) according to Murphy and Riley (1962). Phosphorus forms were separated into NH_4Cl-rP, BD-rP, NaOH-rP, NaOH-nrP, HCl-rP and residual P following, in principle, the sequential extraction scheme suggested by Psenner et al. (1988). These fractions are defined by the extraction method, but ideally each fraction corresponds to a specific phosphorus containing substance within the sediment. Generally, NH_4Cl-rP is regarded as loosely bound phosphorus, BD-rP as phosphorus associated with iron hydroxides, NaOH-rP as phosphorus bound to aluminium, NaOH-nrP as organic phosphorus forms, and HCl-rP as calcium bound phosphorus compounds. Residual P is given by subtracting extracted and identified phosphorus from TP.

The mobile phosphorus fractions in sediments include loosely bound phosphorus, iron bound phosphorus and organic phosphorus forms (Rydin, 2000). These three phosphorus forms typically decrease in concentration with increasing sediment depth (sediment age) indicating a leakage to the overlying water column. This is also reflected in the total phosphorus concentration decreasing with increasing sediment depth. In deeper sediments the phosphorus concentration is typically constant with depth indicating that phosphorus leakage has ceased and only inert phosphorus forms remain.

Loosely bound phosphorus and iron bound phosphorus are closely connected. The iron bound phosphorus is rapidly transformed to loosely bound phosphorus if the sediment turns anoxic. The loosely bound phosphorus may be transported upward by some process (diffusion, bioturbation) and reach the water column. The pool of these inorganic phosphorus forms may vary considerably with season and are the phosphorus forms that leak to the water column contributing to internal loading. The organic phosphorus does not exhibit these seasonal dynamics but is more slowly turned over. However, the organic phosphorus may be mineralized and constitute the original source to the pool of loosely bound and iron bound phosphorus.

Quantifying the pool of mobile phosphorus
To compute the amount of mobile phosphorus per area unit of sediment the phosphorus concentration in deep sediment where sediment diagenesis has ceased, is subtracted from the higher concentrations in more shallow layers. The surpluses in each sediment layer are taken as mobile phosphorus and are integrated over the depth profile to obtain the amount of mobile phosphorus per square metre. The amounts of mobile phosphorus in the fractions of loosely bound, iron bound and organic phosphorus were normalized against mobile total phosphorus. It should be stressed that mobile phosphorus in this context includes all phosphorus that with time will be released as bioavailable phosphorus (phosphate) from the sediments.

Gross deposition in accumulation sediments
Using information about sediment accumulation (g $dw \cdot m^{-2}$) and phosphorus concentration in the settling material deposition rates may be calculated. Removal of phosphorus from the system (burial) is given by sediment accumulation multiplied by the phosphorus concentration in deep sediments. This method slightly overestimates the burial rate since some material (mostly carbon) is lost by respiration decreasing the mass of buried sediment.

Gross deposition is estimated by multiplying sediment accumulation with an estimated phosphorus concentration in settling material. Phosphorus concentration was estimated as the total concentration in surficial sediments with the iron bound phosphorus adjusted to 400 $\mu g\ dw \cdot g^{-1}$ assuming that the actual concentrations of iron bound phosphorus in surficial sediments do not reflect settling concentration but may include upwardly migrating phosphorus originating in deeper sediments trapped in the sediment surface. Our assumption is based on judgement and some experience from lakes, but should if possible of course be supported by analysing settling material.

Release rate
Two methods to estimate the average release rate of phosphorus from the sediments were used. 1) Net burial was subtracted from gross deposition. The difference represents the average release. 2) The size of the mobile phosphorus pool was divided by the age of the sediment layer where the total phosphorus concentration is stabilized. The age of this layer was calculated by dividing the amount of dry material above the layer with the rate of sediment accumulation.

2.3 Results

The collected cores were oxic at the sediment surface except for the sediment collected in Pilkobbsfjärden which showed symptoms of anoxia such as black colour and hydrogen sulphide scent. The sediments from Torsbyfjärden were oxic at the surface but were black around 5 cm down in the sediment, indicating an environmental shift from anoxia to oxic conditions some three years before sampling. As discussed in Part A of this report the recent environmental history of the Stockholm archipelago indicates improved oxygen conditions from the mid 1990s and forward.

In figure 2-2 the water content and the organic content in the different sediment cores are shown. It can be noted that the water content decreases with increasing depth, which is explained by compaction. The organic content also decreases with depth, probably reflecting decomposition rather than changing deposition patterns. In several profiles an anomaly between 10 and 20 cm is present, which may reflect some environmental change that occurred approximately one decade ago. (Accumulation rates range between 1 800 and 2 500 g·m^{-2}·yr^{-1} dw. Assuming a water content of 85 % and an organic content of 20 % this roughly corresponds to between 5 and 7 mm of annual sediment accumulation.)

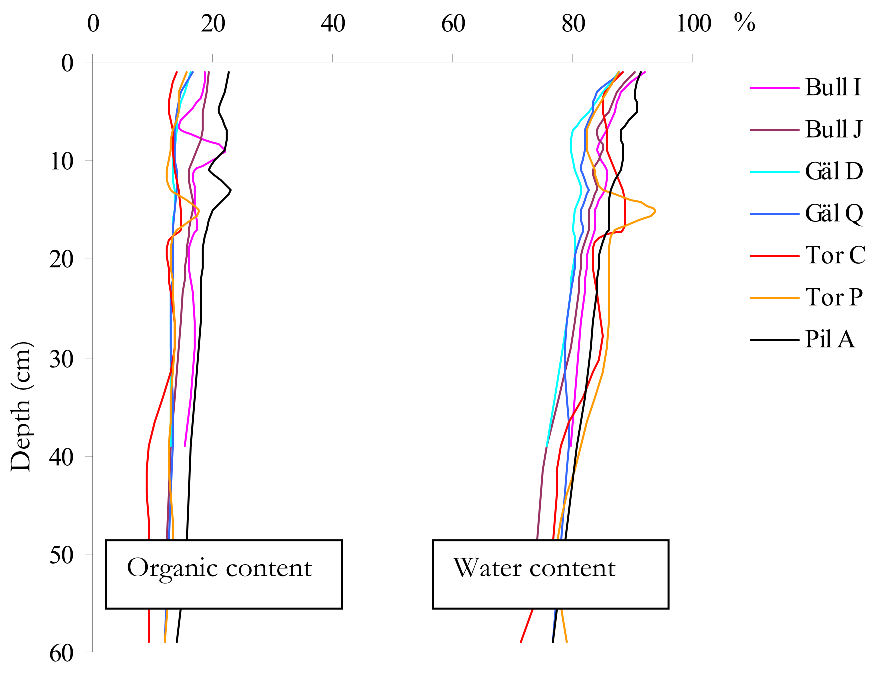
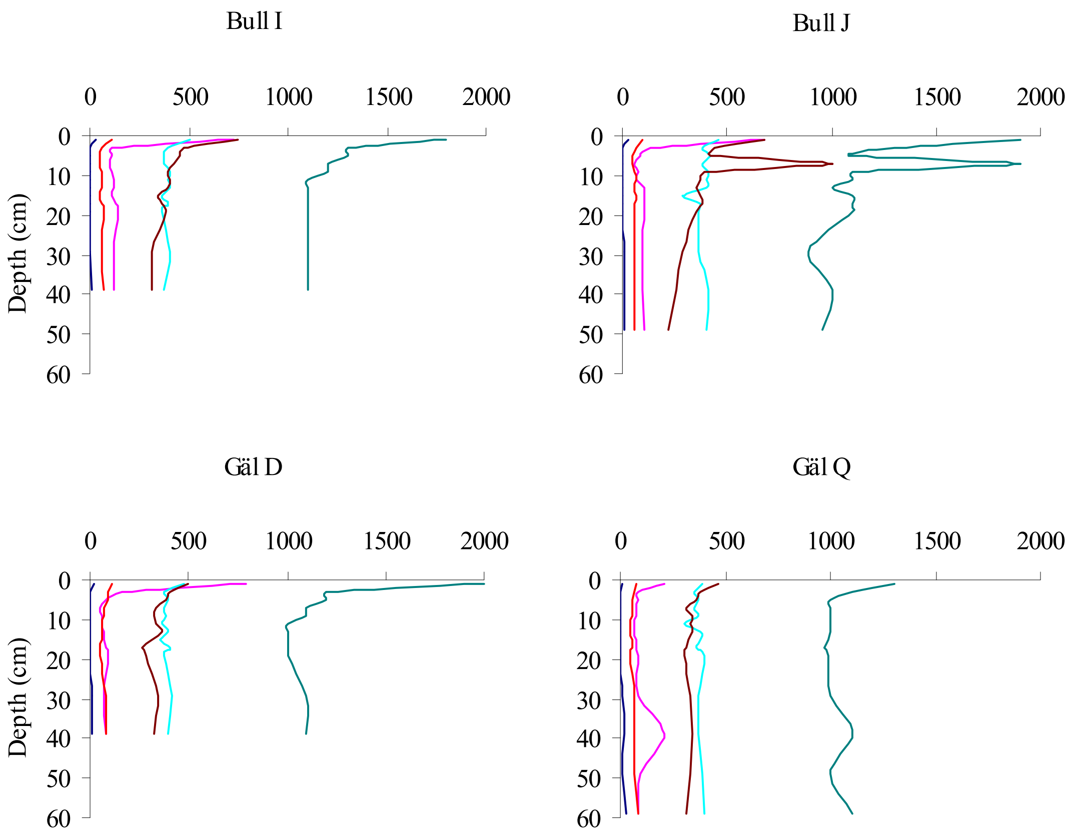


Figure 2-2 Depth profiles of water content and organic content (loss on ignition; %) in the sediment cores.

Profiles of sediment concentration of different phosphorus forms in the collected cores are shown in figure 2-3. Since the 0-2 cm sediment layer represents roughly one year of sedimentation, some labile organic P forms have been mineralized. The organic P concentration measured is therefore underestimated. It can be noted that total sediment concentration decreases with increasing sediment depth. In most profiles the iron bound phosphorus declines rapidly with depth. Apparently very little iron bound phosphorus is present below the top 3-4 cm of sediment, which is probably the depth of the redoxcline. Also the organic phosphorus decreases with sediment depth but less dramatically than the iron bound fraction, reflecting the process of decomposition of organic material. Other P forms are more or less stable with depth. The loosely bound fraction is much smaller than the other, typically around 30 $\mu g \cdot g^{-1}$ dw in surface sediments and decreasing with increasing sediment depth, typically reaching zero concentration a few cm below the surface.



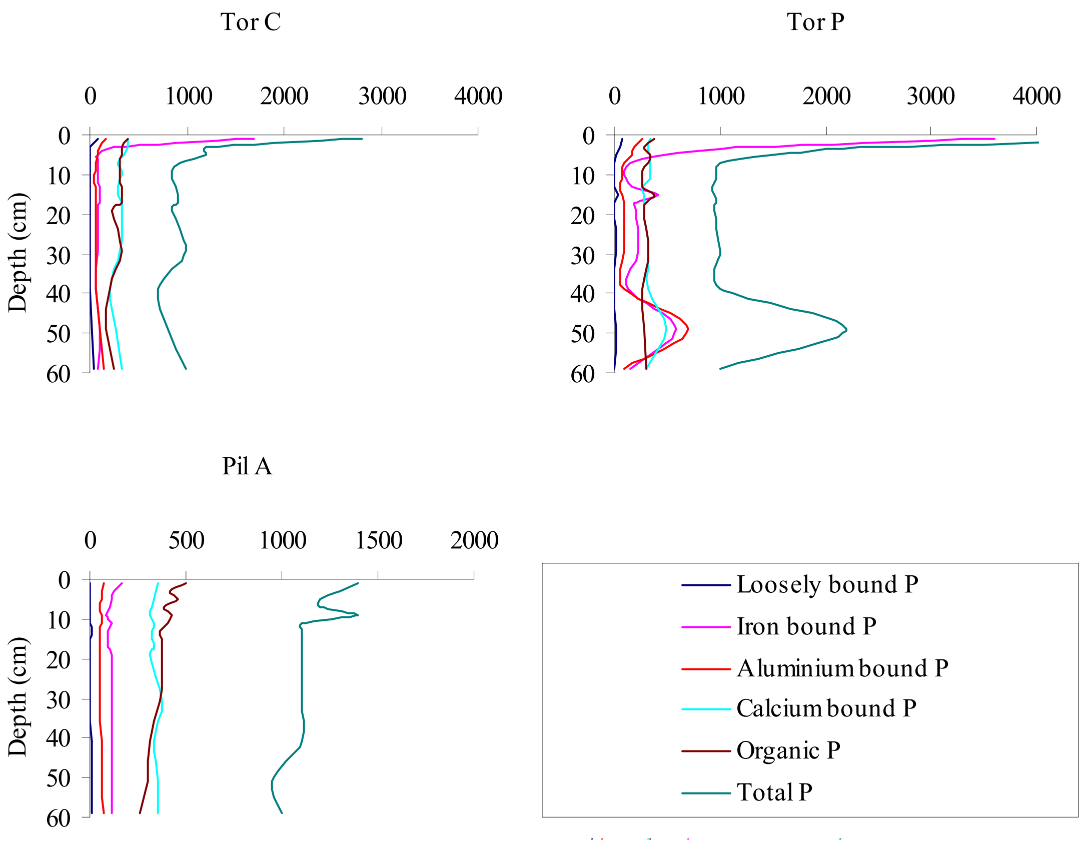


Figure 2-3 Depth profiles of different phosphorus forms ($\mu g \cdot g^{-1}$ dw) in seven sediment cores. Note that the scale for Torsbyfjärden (Tor C and Tor P) is different than in the other graphs. Total P in Tor P surface sediment is 5 600 $\mu g \cdot g^{-1}$ dw.

Total amounts of phosphorus differ considerably between locations, largely explained by the iron bound fraction. Deep sediment total phosphorus concentrations are similar in all cores and around 1 000 $\mu g \cdot g^{-1}$ dw. In particular, Torsbyfjärden exhibits very high concentration of iron bound phosphorus in the surface sediment (3 600 $\mu g \cdot g^{-1}$ dw in Tor P, 0-2 cm), while the iron bound phosphorus concentration in Pilkobbsfjärden is very low (170 $\mu g \cdot g^{-1}$ dw). The sediments in Pilkobbsfjärden were reduced and thus the low iron bound phosphorus concentration was expected. Torsbyfjärden (and Gälnan) has a history of low oxygen concentrations but the situation has recently improved and the sediment surface was oxidized when the cores were collected. The extremely high surface concentrations of iron bound phosphorus may either be upward migrating phosphorus trapped in the oxidized sediment surface or phosphate precipitated from the deep water column at the sediment surface.

Integrated amounts of mobile phosphorus in the different cores are shown in figure 2-4.

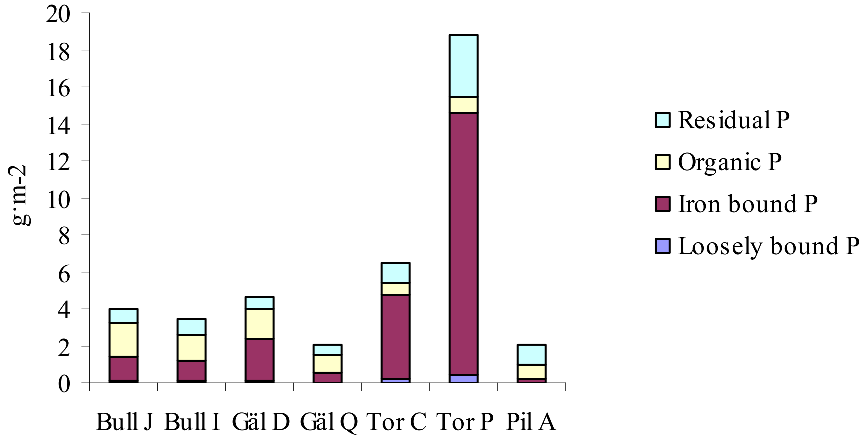


Figure 2-4 Pools of mobile phosphorus in sediment cores from accumulation areas.

The pools of loosely bound phosphorus under oxic conditions were less than 0.1 g·m^{-2} in the sediments from Bulleröfjärden, Gälnan and Pilkobbsfjärden. In the two profiles from Torsbyfjärden the pools were larger, 0.2 and 0.5 g·m^{-2}. As expected from surface concentrations, the largest variation was seen in the iron bound phosphorus pool. In this pool the amounts varied between 0.2 g·m^{-2} (Pilkobbsfjärden) and more than 14 g·m^{-2} (Torsbyfjärden). The total pools of mobile phosphorus varied between 1.4 and 19.4 g·m^{-2}.

These results may be compared with mobile phosphorus in Lake Erken sediments, a naturally eutrophic lake. In Lake Erken most mobile phosphorus is organic (4 g·m^{-2}) while the iron bound phosphorus varies with season between 0.5 and 2 g·m^{-2} (Rydin, 1999). The mobile phosphorus pool in Lake Erken is thus around 5 g·m^{-2}. A comparison with Baltic offshore sediments indicates that phosphorus turnover is larger in coastal sediments than in marine sediments. At 90 m depth in the Landsort deep the total mobile phosphorus pool was less than 4 g·m^{-2}, and the annual release was estimated to 0.04 g·m^{-2}. The pool of mobile organic phosphorus was estimated to 0.5 g·m^{-2} and the annual release from this pool was estimated to between 0.01 and 0.02 g·m^{-2} (Ahlgren, 2006).

Erosion/transport areas

Sediments were collected in three erosion/transportation areas, and samples were taken in the surface layer and in glacial clay material a few cm below the surface. Results from chemical analyses are shown in table 2-1.

Table 2-1 Results from chemical analyses in erosion/transport sediments. Water content and organic content in %; phosphorus concentrations in µg·g^{-1} dw.

	Water content	Organic content	Loosely bound P	Iron bound P	Aluminium bound P	Calcium bound P	Organic P	Total P
Bull (surface)	71	6,4	8	120	38	270	190	950
Bull (glacial)	54	3,0	4	44	100	520	24	640
Gäl (surface)	43	3,3	6	90	18	190	70	630
Gäl (glacial)	38	1,7	1	26	51	450	10	550
Tor (surface)	53	3,2	2	65	22	380	53	680
Tor (glacial)	66	10	5	28	39	450	120	870

Water contents and organic contents are typical of erosion (Gälnan) and transport (Bulleröfjärden, Torsbyfjärden) surface sediments. Total phosphorus concentrations are lower than in accumulation sediments, most notably lower in the iron bound and organic fractions. The low iron bound phosphorus concentration compared with accumulation sediments can be explained both by the fact that the deposited material is coarser with lower total phosphorus content and by the absence of burial processes and subsequent upward migration and surficial trapping of released iron bound phosphorus.

Phosphorus fluxes

Dry material deposition rates were estimated by lamina counting except for Bull J where the deposition rate was taken from Jonsson et al. (2003) due to absence of lamina. The calculated values were as follows: Bull I (1 980 g $dw \cdot m^{-2} \cdot yr^{-1}$), Bull J (2 500 g $dw \cdot m^{-2} \cdot yr^{-1}$), Gäl D (1 960 g $dw \cdot m^{-2} \cdot yr^{-1}$), Gäl Q (1 720 g $dw \cdot m^{-2} \cdot yr^{-1}$), Tor C (3 212 g $dw \cdot m^{-2} \cdot yr^{-1}$), Tor P (1 609 g $dw \cdot m^{-2} \cdot yr^{-1}$) and Pil A (1 597 g $dw \cdot m^{-2} \cdot yr^{-1}$).

Using dry deposition rates and sediment concentrations the deposition and burial rates of phosphorus were calculated as described above. Release of mobile phosphorus was calculated using the two methods described above. In figure 2-5 deposition and release are shown for the seven stations with “Release a” corresponding to release calculated as deposition minus burial and “Release b” corresponding to release calculated as mobile phosphorus divided by turnover time. Agreement between the two methods for calculating release rates is generally acceptable.

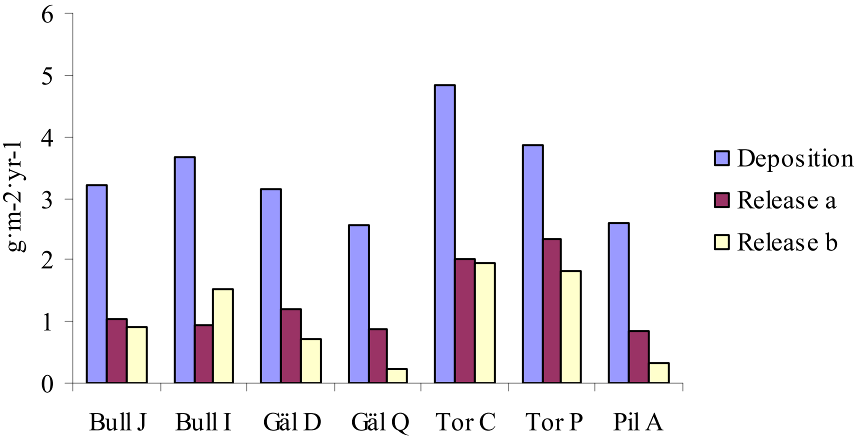


Figure 2-5 Deposition and release rates for the seven accumulation area stations. “Release a” corresponds to release calculated as deposition minus burial and “Release b” corresponds to release calculated as mobile phosphorus divided by turnover time.

Iron and manganese

In surface samples from Torsbyfjärden, both Fe and Mn concentrations were elevated compared to the other samples that were analysed (Table 2-2). However, Mn concentrations were generally two orders of magnitude lower than that of Fe. To evaluate the correlation between Fe and P, we plotted P extracted as iron bound P against Fe in surface (0-2 cm) samples (figure 2-6). A correlation was found, and to calculate the ratio between P associated to Fe, we assumed that all Fe above 48 $mg \cdot g^{-1}$ dw (fig. 2-6) was available for P sorption. Hence, the ratio between “surplus” Fe and “Fe-P” could be calculated. In the two surface samples from Torsbyfjärden, a molar ratio of 15:1 (Fe:P) was found.

Table 2-2 Total amounts of iron and manganese in sediment samples.

	Fe $mg \cdot g^{-1}$ dw	Mn $mg \cdot g^{-1}$ dw
Bull I 0-2	38	0.63
Bull J 0-2	37	0.70
Gäl D 0-2	42	0.47
Gäl Q 0-2	39	0.43
Tor C 0-2	48	0.91
Tor C 2-4	42	0.52
Tor C 8-10	38	0.51
Tor C 18-20	35	0.53
Tor C 58-60	40	0.81
Tor P 0-2	65	1.25
Pil A 0-2	38	0.56
Pil A 2-4	42	0.51
Pil A 8-10	39	0.50
Pil A 18-20	39	0.57
Pil A 60-62	39	0.45

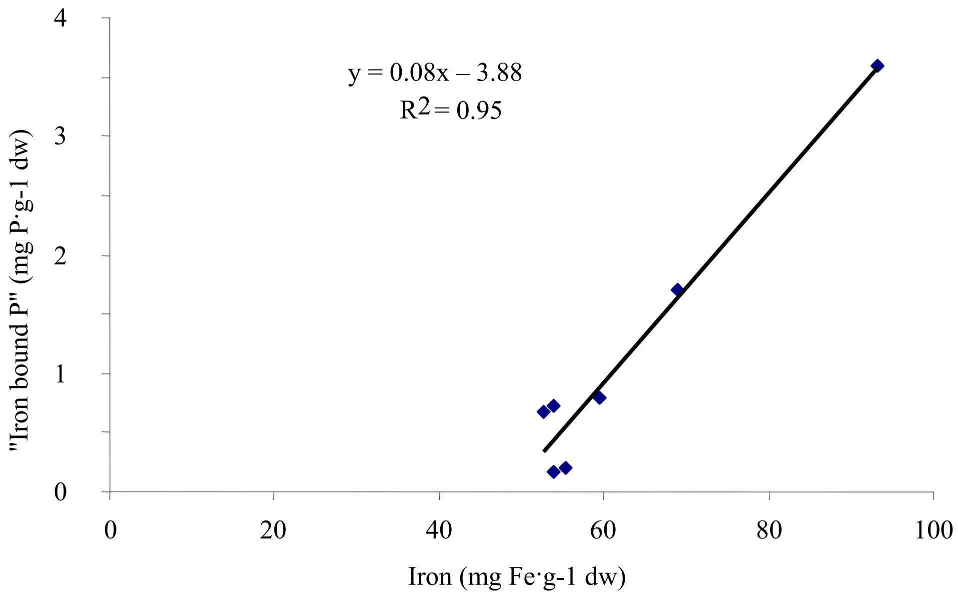


Figure 2-6 Iron bound phosphorus in surficial sediments as a function of iron concentration.

2.4 Discussion

The two approaches used for calculating sediment P release rates should be considered as long term averages, and they both required some assumptions to be made. One of the two approaches, subtracting the yearly burial of P in deeper sediment layers from the amount of P present in the most recent, where the difference corresponds to the released amount per year, requires a correction for the P present in the surface layer. The high concentration of Fe-P present in most of the surface layer samples is most likely not associated with the settling of matter forming the bulk of sediment. More likely, it is an exceptional accumulation of Fe-P under oxic condition discussed below. Therefore, we assume the Fe-P concentration in settling matter to be 400 μg P·g^{-1} dw. Using this concentration, P concentrations in the surface sediment layer average around 1.7 mg P·g^{-1} dw. This is close to the P concentration reported for settling matter outside Himmerfjärden (Blomqvist & Larsson, 1994). Another assumption made is that the average sediment P concentration in each year, as well as the distribution, has been fairly constant over the last two decades. The other method, dividing the mobile P pool with the time period it is present in the sediment profile, calculating its turnover time, also assumes a steady state situation regarding the size of the mobile P pool.

The mobile P pool consists mainly of Fe-P and organic P forms. In the two cores from Torsbyfjärden, Fe-P dominates the mobile P pool (fig. 2-4). In the other cores, organic P forms represent the largest amounts of P to be released. The fraction representing degradable organic P forms declines with depth in all cores, and this decline is assumed to represent degradation/mineralization of organic matter containing P (Ahlgren et al., 2006), most likely autochthonous forms. There seems to be a faster turnover of the organic P pool in the brackish sediment compared to lake sediments. In Lake Erken for instance, the decline in organic P continues down to at least 30 cm before stabilizing (Malmaeus & Rydin, 2006), roughly representing 50 years. In the cores analyzed here, organic P mineralization seems to be finished before 10 cm down in the sediment profile, representing less than a decade of mineralization processes.

Mineralization rate may be calculated using similar methodology as for calculating release rates above. To do this the deposition and burial rates of organic P and the mobile organic P pools substitute rates and pools of total phosphorus in the above calculations. Calculated mineralization rates are presented in table 3. Slower decomposition is generally expected in anoxic environments (e.g. Gächter et al., 1988). The calculated mineralization rates are much larger in Bulleröfjärden than in the other sediments. In particular the decomposition in Tor P and Pil A appear to be relatively slow which may reflect anoxic conditions in recent years (although not the latest years in Torsbyfjärden). However, information about historical changes in deposition of organic material is missing but may influence the apparent mineralization rate calculated with the applied methods. It is notable, however, that mineralized organic P will eventually be released to the water column at different rates in different environments.

Table 2-3 Mineralization rates (g·m^{-2}·yr^{-1}) calculated for the seven accumulation area stations. "Rate a" corresponds to mineralization calculated as deposition of organic P minus burial and "Rate b" corresponds to mineralization calculated as mobile organic phosphorus divided by turnover time.

	Rate a	Rate b
Bull J	0.7	0.8
Bull I	1.0	0.8
Gäl D	0.4	0.2
Gäl Q	0.3	0.2
Tor C	0.4	0.2
Tor P	0.1	0.1
Pil A	0.2	0.1

Organic P turnover is large enough to generally be the main source of P to be released in most sediment cores. The release rates obtained in most cores, about 1 g P·m^{-2}·yr^{-1} (fig. 2-5), and close to 2 g P·m^{-2}·yr^{-1} in Torsbyfjärden, are several times higher than the rates calculated by Luukari (2008) for the Gulf of Finland and Finnish archipelago sites, but she did not include the contribution from mineralization from the organic P pool, and consequently she did state her rates to be minimum rates. However, several cores presented in Luukari (2008) both contained sediment accumulation rates as well as P concentrations similar to the ones obtained in this study. Therefore, using our approach to estimate phosphorus release, about the same rates is likely. Release rates measured by Lehtoranta et al. (2007) in sediments from the Åland archipelago ranging from 0.3 to 2.4 g $P{\cdot}m^{-2}{\cdot}yr^{-1}$ (average 0.8 g $P{\cdot}m^{-2}{\cdot}yr^{-1}$) are compatible with the numbers calculated in this work. Release rates at these levels are also similar to rates from mesotrophic lake sediments (Nürnberg, 1988). P release from eutrophic lake sediments varied between 3 and 10 g $P{\cdot}m^{-2}{\cdot}yr^{-1}$ (op. cit.). It should be noted that the P released is phosphate and it is therefore directly available for primary production when entering the photic zone, in contrast to the external load that, depending on catchment type, only will be available to some extent. Thus, recycling of P from the sediments investigated in this study, corresponding to 1 tonne of phosphate-$P{\cdot}km^{-2}{\cdot}yr^{-1}$, will be a major factor determining trophic status.

The mobile P pool is present in sediment layers not older than a decade in our investigated cores. This does not exclude that a significant portion of the P pool entered the system several decades ago, i.e. before tertiary treatment was installed in municipal sewage treatment plants, assuming a continuous recycling of bioavailable P. With limitations in burial processes, the only possible other main loss process would be export to the open Baltic Sea.

Mn concentrations are considerably lower than the redox sensitive P (Appendix), and seem therefore not to be of significant importance for P retention. This is in contrast to Fe, that showed almost a doubling in concentration in the two samples from Torsbyfjärden (tab. 2-2), and the increase in Fe showed a constant ratio with redox sensitive P forms. The obtained 15:1 (molar) ratio might seem high compared to reported values as low as 2:1 (Blomqvist et al., 2004) under optimal conditions. However, the same ratio found in these two stations indicates that available sites for phosphate sorption are used, and that the absence of available Fe limits further binding of P. It should be noted though, that the "Fe-P" concentration, and the resulting increase in TP found in Tor P, can be considered very high. Such high values have not, to our knowledge, previously been reported from either fresh or marine systems.

An important question is the source of this surplus Fe and associated P. It could either be a precipitation of dissolved phosphate and reduced Fe, transported by upward diffusion from deeper and anoxic sediment layers, to the oxidized surface layer where it accumulates. The phosphate could originate from e.g. mineralization of biogenic P forms in deeper sediment layers. Or it could reflect settling of Fe-P rich compounds, freshly precipitated in the water column. Both these patterns would follow the classical pattern suggested by Mortimer (1941). Besides precipitation in the water column, and subsequent settling, larger particles rich in Fe-P forms possibly resuspended from other sediment sites, could explain the observed pattern.

One attempt to determine whether the high amount of the Fe-P complex present in Tor P surface sediment can be a result of migration from deeper sediment layers is to assume that the release since the surface sediment turned oxic has accumulated in the surface sediment instead of being released. Using the calculated release rates for Tor P (fig. 2-5), 2 g $P{\cdot}m^{-2}{\cdot}yr^{-1}$, and assuming an oxic time period of 3 years, 6 g of P associated to Fe could have accumulated in the surface layer. In addition, some Fe-P in settling matter should be included in the 14 g of "Fe-P" stored in the Tor P core. Although some assumptions have to be made, therefore giving uncertain numbers, we cannot rule out the underlying sediment as a major source of P (and Fe) to the large pool of Fe-P in the Tor P core.

Regardless of which of the possible pathways suggested above dominates quantitatively, significant amounts of phosphate have been trapped in the surface sediment layers due to its oxygenated status, and instantly bioavailable P has been withdrawn from primary production. It is, however, a temporary storage. This Fe-P rich layer will be covered by new sediment, eventually turning the present surface layer anoxic as it ages, and dissolving the Fe-P complexes that will migrate towards the sediment surface. Depending on future surface sediment oxygen status, Fe-P will either precipitate again if the surface is oxygenated, or leak to the water column if anoxic. Even if the sediment surface is maintained oxic, there is a limited amount of Fe-P that can be stored in the surface sediment layer. Thus, we cannot rule out that even under oxic conditions, P is released from the sediment.

It has been argued (Gunnars and Blomqvist, 1997) that the limited presence of iron may hold back precipitation of Fe-P in oxygenated bottom waters, implying that release of Fe-P from surface sediments turning anoxic is not reversible, see also Blomqvist et al., (2004). If precipitation of Fe-P has occurred in Torsbyfjärden as indicated above this would contradict the findings by Gunnars and Blomqvist (1997). Ongoing studies of oxygenating bottom waters in Baltic coastal areas may provide further insight into this problem.

The P deposition is larger than the estimated release in all examined cores, which is the only sustainable situation in a steady state. There are, however, indications that the sediments may temporary act as net sources of phosphorus (see, e.g., part A of this report), which is only possible if the release lags after a previous loading of the sediments. The deepest part of the archipelago where many of the examined cores were collected was probably anoxic during long periods and may thus have lost much of the redox sensitive P to the water column. More shallow areas may contain more of these fractions and hence release more phosphorus to the water column. Organic phosphorus, on the other hand, seems to have a slower turnover particularly in anoxic sediments, and could possibly accumulate in amounts large enough to support a subsequent net release following a period of large deposition. Although this is not indicated in the examined cores it may occur locally also in the Stockholm archipelago.

The sediments in the different areas of this study differ in several respects but it may still be meaningful to make comparisons. The mobile phosphorus pools are very different, and the fates of these pools are of major importance for the water quality in the coastal areas. 1 $g \cdot m^{-2}$ corresponds to 1 $tonne \cdot km^{-2}$, apparently characterizing the difference in mobile P pools between oxic areas such as Bulleröfjärden and anoxic areas such as Pilkobbsfjärden. The total area of the Stockholm archipelago is around 3 000 km^2 with a significant proportion of accumulation areas implying that the sediments probably contain in the order 10^3 tonnes of mobile phosphorus with unknown destination. Extrapolation of numbers to the Baltic Proper should not be done carelessly, but the pool of mobile phosphorus must be orders of magnitudes larger than the pool inside the Stockholm archipelago. More certain is that the pool of phosphorus in the water column of the Baltic Proper is around 500 000 tonnes (Savchuk, 2005) and the annual riverine inflow is around 16 000 tonnes (HELCOM, 2004). As exemplified in Part A of this report the P release from accumulation areas of the Stockholm inner archipelago are of the same magnitude or even larger than the outflow from Lake Mälaren. On the other hand coastal sediments may also serve as an efficient sink of phosphorus through sediment burial. In this perspective the uncertainties in our calculations regarding sediment release of mobile phosphorus are amplified from fractions of grams per square meter into thousands of tonnes in the Baltic Sea. The scope of implications certainly motivates further studies of pools and fluxes of mobile phosphorus in Baltic Sea sediments.

2.5 Conclusions

The magnitude of sediment phosphorus (P) turnover in the Stockholm archipelago is closely linked to the sediment accumulation rate. Improvement of the oxygen status in the surface sediment layer results in a temporary accumulation of iron (Fe) bound P. This P might reach high concentrations, and represents a withdrawal of P that otherwise would support primary production. Whether this Fe-P mainly did precipitate in the water column and did settle to the sediment, or if it formed in the oxygenated surface sediment layer due to diffusion of dissolved P and Fe from deeper sediment layers remains uncertain.

In cores from Gälnan, Bullerö-, Torsby-, and Pilkobbsfjärden, gross deposition of P varied between less than 3 to near 5 $g \cdot m^{-2} \cdot yr^{-1}$, after correction for Fe-P accumulation, burial concentrations of P occurred already after between 2 and 10 years, and burial fluxes was measured to between 1,5 and 3 g $P \cdot m^{-2} \cdot yr^{-1}$. Sediment mobile P, mainly organic P and Fe-P, varied between less than 2 and up to 19 $g \cdot m^{-2}$. P to be released was calculated using two different approaches and yearly release rates between 0.2 and 2 g $P \cdot m^{-2}$ were obtained. These rates should be considered as minimum rates. The concentration and composition of P settling out from the water column at different seasons and sites needs to be determined to improve our estimates of P turnover in the archipelago. The redox sensitive P pools varied between around 0.2 and 14 $g \cdot m^{-2}$ (a factor of 60) reflecting alternative distributions of phosphorus between water and sediment. Extrapolated to the entire archipelago the accumulation sediments likely contain several thousand tonnes of mobile phosphorus.

All examined sediments appear to be net sinks of phosphorus. This does not exclude however, that sediments locally may act as temporary net sources of phosphorus, as indicated by mass-balances in Part A of this report. To support such a suggestion, however, requires further studies in a larger sampling area, including sediments from a range of water depths and bottom dynamics.

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Appendix Primary data from phosphorus fractionation of sediments

Station	Layer	NH4Cl-rP	BD-rP	NaOH-rP	NaOH-nrP	HCl-rP	Res-P	Total P	Water content	Loss on ignition
Position		*Losely bound P*	*Fe-P*	*Al-P*	*Organic P*	*Ca-P*		TP		
WGS 84	cm	µg P/g TS							%	
Bull J Lat 591157 Long 184951 Depth 44m	0-2	27	730	110	750	510	-357	1800	92	19
	2-4	5	110	58	470	390	280	1300	88	18
	4-6	1	110	52	450	370	290	1300	87	16
	6-8	0	100	54	420	370	210	1200	86	15
	8-10	0	110	56	390	400	200	1200	84	22
	10-12	5	120	58	400	390	170	1100	86	17
	12-14	0	120	64	390	400	150	1100	85	17
	14-16	0	110	55	340	360	260	1100	84	17
	16-18	0	130	62	360	390	190	1100	84	17
	18-20	0	140	67	380	360	180	1100	83	16
	28-30	3	120	59	310	400	240	1100	81	17
	38-40	10	120	69	310	370	190	1100	80	15
Bull I Lat 591152 Long 184941 Depth 47m	0-2	32	680	99	680	460	-55	1900	90	19
	2-4	3	130	63	440	380	270	1300	87	19
	4-6	0	83	51	420	420	170	1100	86	18
	6-8	0	59	51	1000	380	360	1900	84	18
	8-10	0	79	56	390	410	170	1100	85	17
	10-12	0	71	68	370	400	170	1100	83	16
	12-14	0	110	54	350	400	86	1000	84	16
	14-16	0	110	63	370	290	270	1100	83	17
	16-18	1	110	53	380	370	170	1100	83	16
	18-20	2	110	56	350	360	200	1100	82	16
	28-30	11	100	56	290	360	66	890	80	14
	38-40	11	97	55	260	410	180	1000	76	13
	48-50	9	110	54	220	400	180	960	74	12

Station	Layer	NH4Cl-rP	BD-rP	NaOH-rP	NaOH-nrP	HCl-rP	Res-P	Total P	Water content	Loss on ignition
Position		*Losely bound P*	*Fe-P*	*Al-P*	*Organic P*	*Ca-P*		TP		
WGS 84	cm	µg P/g TS							%	
	0-2	24	790	110	500	480	120	2000	88	16
	2-4	0	160	95	410	380	160	1200	85	15
	4-6	5	82	87	390	400	180	1200	83	14
Gäl D	6-8	4	53	70	340	380	220	1100	80	14
Lat	8-10	2	61	68	320	390	220	1100	80	14
593130	10-12	2	60	60	330	370	200	1000	80	13
Long	12-14	1	76	60	370	400	100	1000	81	14
184535	14-16	0	70	61	310	360	200	1000	80	14
Depth	16-18	1	77	54	260	410	210	1000	80	13
27m	18-20	2	91	52	280	380	210	1000	80	13
	28-30	12	74	78	350	420	150	1100	78	13
	38-40	12	86	81	320	400	170	1100	76	13
	0-2	6	210	80	470	390	140	1300	88	17
	2-4	2	83	69	380	350	210	1100	84	15
	4-6	2	86	61	360	370	150	1000	83	14
	6-8	0	75	55	310	350	220	1000	82	14
Gäl Q	8-10	0	78	56	340	370	160	1000	82	14
Lat	10-12	1	62	52	330	300	280	1000	81	14
593150	12-14	0	70	50	340	380	180	1000	83	14
Long	14-16	1	78	55	320	380	150	990	81	14
184581	16-18	0	79	53	310	360	170	970	82	13
Depth	18-20	0	81	52	300	400	150	990	81	13
31m	28-30	9	84	67	330	370	160	1000	79	13
	38-40	15	210	71	340	370	66	1100	79	13
	48-50	12	92	67	330	390	130	1000	78	13
	58-60	27	90	85	310	400	160	1100	77	12

Station	Layer	NH4Cl-rP	BD-rP	NaOH-rP	NaOH-nrP	HCl-rP	Res-P	Total P	Water content	Loss on ignition
Position		*Losely bound P*	*Fe-P*	*Al-P*	*Organic P*	*Ca-P*		TP		
WGS 84	cm	µg P/g TS							%	
Tor C Lat 592040 Long 182776 Depth 31m	0-2	73	1700	170	390	390	130	2800	88	14
	2-4	3	250	100	330	400	67	1200	85	13
	4-6	0	82	73	330	350	320	1200	85	13
	6-8	0	73	64	300	280	220	930	86	13
	8-10	0	85	60	310	320	74	850	86	13
	10-12	0	84	50	300	300	100	840	87	14
	12-14	0	95	55	340	290	100	890	88	14
	14-16	0	96	62	320	280	150	900	89	15
	16-18	0	99	63	330	320	110	910	88	15
	18-20	0	82	59	230	330	140	840	83	12
	28-30	5	92	68	330	300	180	980	85	14
	38-40	2	68	54	210	210	160	700	78	9
	49,00	13	100	100	160	270	160	810	77	9
	59,00	31	81	150	240	320	150	980	71	9
Tor P Lat 592168 Long 182704 Depth 52m	0-2	71	3600	270	370	350	980	5600	88	16
	2-4	59	1300	190	280	330	290	2500	86	14
	4-6	11	480	170	340	340	190	1500	84	14
	6-8	0	150	87	330	340	110	1000	82	13
	8-10	0	95	73	270	350	170	960	82	13
	10-12	0	110	71	260	340	190	970	84	12
	12-14	0	170	66	270	270	140	920	85	13
	14-16	37	410	67	380	290	-254	940	94	18
	16-18	0	190	87	300	290	91	960	87	14
	18-20	0	200	90	280	280	99	950	86	13
	28-30	14	220	86	330	330	17	1000	86	14
	38-40	3	140	100	260	330	180	1000	81	13
	48-50	11	590	700	290	500	110	2200	77	13
	58-60	0	160	99	300	310	130	1000	79	12

Station	Layer	NH4Cl-rP	BD-rP	NaOH-rP	NaOH-nrP	HCl-rP	Res-P	Total P	Water content	Loss on ignition
Position		*Losely bound P*	*Fe-P*	*Al-P*	*Organic P*	*Ca-P*		TP		
WGS 84	cm	µg P/g TS							%	
Pil A Lat 591132 Long 184521 Depth 58m	0-2	0	170	71	500	350	280	1400	91	23
	2-4	0	120	61	420	340	340	1300	90	22
	4-6	0	110	64	460	330	220	1200	91	21
	6-8	0	99	53	390	320	320	1200	88	22
	8-10	0	84	58	430	310	510	1400	88	22
	10-12	0	110	60	410	330	240	1100	88	19
	12-14	9	95	49	360	320	240	1100	86	23
	14-16	0	97	54	370	320	260	1100	86	20
	16-18	0	90	56	370	330	270	1100	86	19
	18-20	0	110	53	370	310	280	1100	85	18
	30-32	3	110	55	360	370	200	1100	83	18
	40-42	9	110	62	310	330	240	1100	81	16
	50-52	11	110	65	300	350	110	950	79	16
	60-62	15	110	73	260	350	180	1000	77	14

Bull ET1 Depth 17m	surface	8	120	38	190	270	330	950	71	6
	glacial	4	44	100	24	520	-54	640	54	3
Gäl ET1 Depth 15m	surface	6	90	18	70	190	250	630	43	3
	glacial	1	26	51	10	450	12	550	38	2
Tor ET1 Depth 12m	surface	2	65	22	53	380	150	680	53	3
	glacial	5	28	39	120	450	220	870	66	10

Bull ET1: Lat 591185 Long 184867 Gäl ET1: Lat 593130 Long 184561 Tor ET1: Lat 592050 Long 184561